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GENERALIZED THEORY OF INTERFERENCE, AND ITS APPLICATIONS

Part I. Coherent Pencils

By S. Pancharatnam

(*Memoir No. 88 of the Raman Research Institute, Bangalore-6*)

Received October 30, 1956

(Communicated by Sir C. V. Raman)

§ 1. Introduction

The investigations of which the results are presented in this paper arose during the study of certain specific problems in crystal optics. As investigators in this field are well aware, the simplest procedures for studying the optical properties of anisotropic media (*e.g.*, examination under the polarising microscope) generally involve the use and study of polarised light. The complexity of the peculiar interference phenomena exhibited and also of their customary theoretical analysis (by algebraic methods) become quite considerable even in the case of transparent optically active crystals like quartz—as may be seen by a reference to the treatises of Mascart (1891) and Walker (1904); this is because the two waves propagated along any direction in such a medium are no longer linearly polarised at right angles to one another, but are elliptically polarised. Nevertheless, the types of 'oppositely' polarised waves propagated in such media must be termed simple compared to the elliptically polarised waves propagated in *absorbing biaxial crystals*.

The remarkable interference phenomena exhibited by absorbing biaxial crystals may be easily studied by looking at an extended source through a plate (cut normal to an optic axis); a suitable material is the mineral iolite—which the author had the opportunity of investigating experimentally (Pancharatnam, 1955). (1) With the incident light polarised, and *even without the use of an analyser*, interference rings are seen, which are feeble but are nevertheless easily visible. (2) When, in addition, an analyser is also introduced, the biaxial interference figures seen are notably different from those seen in transparent crystals under the same conditions. (3) With the analyser in position and with no polariser—*i.e.*, *with the incident light completely unpolarised*—feeble interference rings are again easily visible. (4) Finally, even when both analyser and polariser are absent, incipient traces of an interference pattern may be discerned.

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Viewing these particular phenomena from a slightly broader perspective we see that their analysis is connected with certain general questions concerning the properties of two polarised beams travelling along the same direction. We shall now formulate these problems since they form the main content of the paper. The study of the effects with a polariser alone leads us to investigate the following questions: the interference of two coherent beams in different states of elliptic polarisation (§ 3); the resolution of any polarised beam into two beams in given states of polarisation—which occurs at the first face of the crystal plate (§ 4); and the composition of two coherent beams of different polarisation—at the second face of the plate (§§ 5, 6). The problem involved when an analyser is also introduced (keeping the incident light polarised) reduces to the following: the interference of two coherent polarised beams which are ' brought to the same state of elliptic vibration ' by the use of a suitable analyser (§ 8). In § 9 we shall consider the addition of n coherent beams in different states of polarisation.

An attempt to formulate in general terms the problems associated with (3) and (4) leads rather unexpectedly into the subject of the partial coherence of polarised beams. We shall leave the discussion of this subject for Part II.

§ 2. THE POINCARÉ SPHERE AND THE STOKES PARAMETERS

For problems—such as the one we are dealing with—where we require to handle elliptic vibrations with the same facility as linear vibrations, the indirect specification of the polarisation of an elliptic vibration by giving the equation to its rectangular components is obviously unsatisfactory: the procedure not only leads to cumbersome calculations lacking in elegance, as has been pointed out by other authors, but often ceases to give physical insight into the cause of the phenomena actually observed. Two other powerful methods for specifying the state of polarisation of a beam have been used extensively—an analytical method due to Stokes (1901), and a geometrical one due to Poincaré. The conventional theoretical presentation of the subject of the ' Stokes parameters ' may be found in Chandrasekhar (1949) and in Rayleigh (1902); that of the Poincaré sphere and some of its more well-known properties may be found in Pockels (1906), Walker (1904), Ramachandran and Ramaseshan (1952), and Jerrard (1954). In Part I of the present paper, only the Poincaré representation is used; and we may mention that this part constitutes in itself a self-contained derivation of the properties of the Poincaré sphere by a new procedure. The Stokes representation will be required only in Part II where the subject of partial polarisation naturally enters; but the entire subject of the Stokes representation is introduced there,

in a new manner, through the Poincaré representation itself—by developing the ideas of Fano (1949) and Ramachandran (1952).

The state of polarisation of a completely polarised beam is directly specified by the form of the ellipse traced by the tip of the displacement vector—this being invariant for a completely polarised beam, unlike the intensity and absolute phase which may be subject to statistical fluctuations. Poincaré introduced a mapping whereby any particular form of elliptic vibration is represented by a specific point on the surface of a sphere—the points on the ' Poincaré sphere ' exhausting all the conceivable forms of elliptic vibrations. The definition of the mapping allows the ellipse represented by a point P to be visualised directly in terms of the longitude 2λ and latitude 2ω of the point: for λ is the azimuth of the major axis of the elliptic vibration and $\tan \omega$ the ellipticity. Alternatively the point P may be specified in cartesian co-ordinates instead of in polar co-ordinates—with the XY plane coinciding with the equatorial plane. As Perrin (1942) had observed, the *three parameters introduced by Stokes for characterising a completely polarised beam are proportional to the cartesian co-ordinates of the point P*—the constant of proportionality being the intensity of the beam which is taken as the fourth Stokes parameter.

Two elliptical vibrations whose states of polarisation are represented by diametrically opposite points on the Poincaré sphere will be said to be oppositely polarised. The conventional procedure of decomposing any elliptic vibration into two rectangular linear vibrations (represented by two diametrically opposite points on the equator) is a particular case of decomposing it into two elliptical vibrations of opposite polarisation. The fundamental property of the Poincaré sphere relates to such a decomposition (*see* Fig. 1) and is the following:—

I. *When a vibration of intensity I in the state of polarisation C is decomposed into two vibrations in the opposite states of polarisation A and A', the intensities of the 'A-component' and the 'A'-component' are* $I \cos^2 \frac{1}{2} CA$ *and* $I \sin^2 \frac{1}{2} CA$ *respectively.*

All the results proved in this paper are deduced from the above theorem. We shall not give the proof of the theorem since a proposition equivalent to the above has been proved by other authors (*see* § 8 below).

Since according to Theorem I, the sum of the intensities of the oppositely polarised component beams are together equal to the intensity I of the resultant beam we deduce the following well-known result.

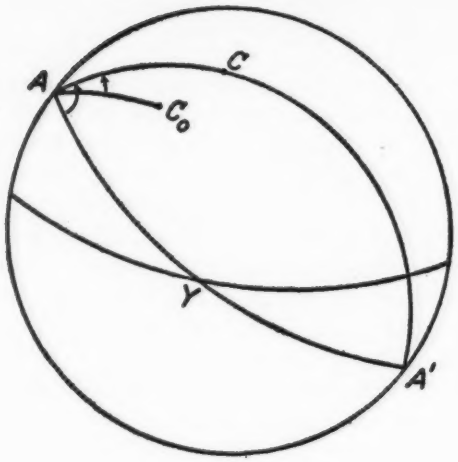

FIG. 1

II. *Two oppositely polarised beams cannot constructively or destructively interfere.*

§ 3. INTERFERENCE OF TWO NON-ORTHOGONALLY POLARISED VIBRATIONS

The interference of two *linear* vibrations not orthogonal to one another can be analysed by resolving the first vibration into two vibrations which are respectively parallel and orthogonal to the second vibration. The interference of any two elliptically polarised vibrations will now be handled in a similar manner. We shall prove the following proposition.

III. The intensity I of the beam obtained on combining two mutually coherent beams 1 and 2, of intensities I_1 and I_2 in the states of polarisation A and B respectively, will be given by the general interference formula:—

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \tfrac{1}{2}c \cos \delta \qquad (1)$$

Here c is the angular separation of the states A and B on the Poincaré sphere (*see* Fig. 2). Thus $\cos^2 \frac{1}{2}c$ is a ' similarity factor ' between the states of polarisation, which determines the extent of interference and which varies from unity (for identically polarised beams) to zero (for oppositely polarised beams). The significance of the ' phase difference ' δ between the beams will be elucidated below.

The above relation may be obtained as follows. The vibration 2 may be replaced by two oppositely polarised vibrations—one in the state of polarisation A of the first beam, and the second in the state of polarisation A′ orthogonal to A. These vibrations (which we shall denote by 2_A and $2_{A'}$ res-

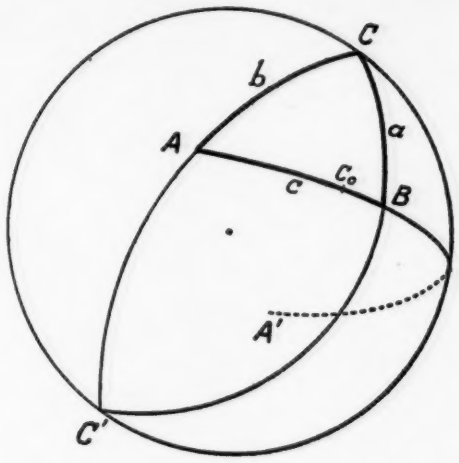

FIG. 2

pectively) will be coherent with vibration 1 and will have intensities $I_2 \cos^2 \frac{1}{2}c$ and $I_2 \sin^2 \frac{1}{2}c$ respectively (§ 2, I). The vibration 1 being in the same state of polarisation as vibration 2A (over which it has a phase advance δ, say), can be combined with it to yield a vibration $(1 + 2A)$ of intensity

$$I_1 + I_2 \cos^2 \tfrac{1}{2}c + 2\sqrt{I_1 I_2} \cos \tfrac{1}{2}c \cos \delta$$

We are thus left with the vibration $(1 + 2A)$ and the vibration $2A'$ which are in the opposite states of polarisation A and A′. The resultant intensity I, obtained merely by adding their intensities (§ 2, II), is that given in formula (1) which we wished to deduce.

An explicit expression for the similarity factor between any two states of polarisation (in terms of the azimuths λ_1, λ_2 of the major axes and the ellipticities $\tan \omega_1$, $\tan \omega_2$ of the two vibrations) may, if necessary, be obtained from the following relation (obtained by spherical trigonometry):—

$$\cos c = \sin 2\omega_1 \sin 2\omega_2 + \cos 2\omega_1 \cos 2\omega_2 \cos 2(\lambda_2 - \lambda_1) \qquad (2)$$

It may be noted that $\cos \frac{1}{2}c$ is equal to the visibility of fringes (as defined by Michelson) obtained under the conditions $I_1 = I_2$.

In the above discussion the quantity δ has been introduced as the phase advance of the first beam over the A-component of the second beam. There are two properties of δ however which enable us to speak of it as the absolute difference of phase between the two beams themselves—though they are in different states of polarisation. In the first place we note that if the first

beam is subjected to a particular path retardation relative to the second, then δ as defined above decreases by the corresponding phase angle; in the second place we note that as long as no path retardation is introduced between the two beams, any alteration of the intensities of the two beams will not change the value of δ as defined above. Hence we will be guilty of no internal inconsistency if we make the following statement by way of a definition: *the phase advance of one polarised beam over another* (not necessarily in the same state of polarisation) *is the amount by which its phase must be retarded relative to the second, in order that the intensity resulting from their mutual interference may be a maximum.*

This phase advance is identically equal to δ, and the above definition holds only for non-orthogonal vibrations.

By picturing an elliptic vibration as being made up of its rectangular components, it becomes apparent that the coherent addition contemplated in this section, of two beams in different states of polarisation will yield a resultant beam which is also elliptically polarised. The intensity of this having been determined, the next step logically would be to determine its state of polarisation. This problem we shall relegate to § 5, and take up in the next section the converse problem which is simpler to handle.

§ 4. Decomposition of a Polarised Beam into Two Beams in Given States of Polarisation

The method of approaching the general problem described in the heading is immediately made clear by regarding the following particular case, illustrated in Fig. 3. Suppose that a *linear* vibration C has to be split into two *linear* vibrations A and B (with which it makes angles $\frac{1}{2}b$ and $\frac{1}{2}a$ respectively). The intensities of the A- and B-vibrations may be obtained by the parallelogram law; more specifically, by equating the projections of the B- and C-vibrations in the direction orthogonal to the A-vibration, we obtain the intensity of the B-vibration as proportional to $(\sin \frac{1}{2}b/\sin \frac{1}{2}c)^2$, where $\frac{1}{2}c$ is the angle between the A and B vibrations.

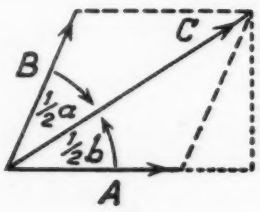

FIG. 3

By similar reasoning we shall prove the following proposition.

IV. If a beam of intensity I in the state of polarisation C is decomposed into two coherent beams 1 and 2, in the states of polarisation A and B respectively, the intensities of these beams will be given by

$$I_1 = I \cdot \frac{\sin^2 \frac{1}{2}a}{\sin^2 \frac{1}{2}c}; \qquad I_2 = I \cdot \frac{\sin^2 \frac{1}{2}b}{\sin^2 \frac{1}{2}c} \tag{3}$$

where a, b and c are the angular separations BC, CA and AB respectively (*see* Fig. 2).

To prove the proposition, we decompose each vibration into two vibrations of polarisation A and A′. The sum of the A′-components of the vibrations 1 and 2 must together be the same as the A′-component of the given vibration 3. The vibration 1, however, has no A′-component since we have chosen A′ opposite to A. Hence the A′-components of vibrations 2 and 3 are identical. Equating their intensities (as given by § 2, I) we have $I_2 \sin^2 \frac{1}{2}c = I \sin^2 \frac{1}{2}b$. Similarly, we can show that $I_1 \sin^2 \frac{1}{2}c = I \sin^2 \frac{1}{2}a$, thus establishing relations (3) above. [The expressions (3) for the intensities I_1 and I_2 could be written explicitly in terms of the constants of the elliptic vibrations by substituting the expression (2) for $\cos c$ and similar expressions, obtained by cyclic permutation, for $\cos a$ and $\cos b$. It can thus be shown that the expressions (3) are equal to the more lengthy expressions deduced directly by Stokes (*loc. cit.*).]

The beams 1 and 2 will have a definite phase relationship with one another which, as we shall see, depends in a remarkable fashion on the mutual configuration of the points A, B and C.

From (1) we have

$$\cos \delta = \frac{I - (I_1 + I_2)}{2\sqrt{I_1 I_2} \cos \frac{1}{2}c}$$

Substituting for I_1 and I_2 from (3),

$$-\cos \delta = \frac{\sin^2 \frac{1}{2}a + \sin^2 \frac{1}{2}b - \sin^2 \frac{1}{2}c}{2 \sin \frac{1}{2}a \sin \frac{1}{2}b \cos \frac{1}{2}c} \tag{4}$$

If C′ be the point diametrically opposite to C (Fig. 2), then denoting by a', b', c the sides of the triangle ABC′, we will have

$$-\cos \delta = \frac{\cos^2 \frac{1}{2}a' + \cos^2 \frac{1}{2}b' + \cos^2 \frac{1}{2}c - 1}{2 \cos \frac{1}{2}a' \cos \frac{1}{2}b' \cos \frac{1}{2}c}$$

The expression on the right-hand side is the cosine of half the solid angle subtended by the triangle C′BA at the centre of the sphere (*see* M'Clelland and

Preston, 1897, Part II, Ch. 7, p. 50, Ex. 1). Since the Poincaré sphere has unit radius, we arrive at the following unexpected geometrical result.

V. When a beam of polarisation C is decomposed into two beams in the states of polarisation A and B respectively, the phase difference δ between these beams is given by

$$|\delta| = \pi - \tfrac{1}{2}|E'| \qquad (5\,a)$$

where the angle $|E'|$ is numerically equal to the area of the triangle C'BA colunar to ABC. (E' is also the spherical excess of the triangle C'BA, *i.e.*, the excess of the sum of its three angles over π.)

Hitherto we have fixed the state of zero phase difference between two non-orthogonally polarised beams by the criterion that the resultant intensity produced by mutual interference should be a maximum. We can equally well use the fact (shown by relation 5 *a*) that *the beams in the state of polarisation A and B will have zero phase difference when the resultant state of polarisation C* (produced by their mutual interference) *lies on the arc directly joining A and B* (for then the colunar triangle will have the area of a hemisphere). On the other hand, the beams will be opposed in phase ($\delta = \pm\pi$), when the resultant state of polarisation C lies on the *greater* segment of the great circle through A and B (colunar triangle has zero area).

The relation (5 *a*) does not give the sign of δ—the phase advance of vibration 1 over vibration 2. We shall now resolve this ambiguity. It is clear (from considerations of continuity) that the sign of δ remains the same for all positions of the resultant polarisation C lying on any one side of the great circle AB, the magnitude of δ being between 0 and π; and that δ changes sign (without discontinuity) as the resultant polarisation C crosses from one side of the great circle AB to the other. (This is forced by the physical requirement that the addition of the beams 1 and 2 with specific intensities and a specific phase relationship should lead unambiguously to a unique state of polarisation C of the resultant beam.) We can now show that the phase advance of vibration 1 over 2 will be positive if (as is drawn in Fig. 2) the point C appears to the left of AB as we proceed from A to B on the surface of the sphere. To prove this proposition it is sufficient to show that this rule of signs is true for a *particular* pair of non-orthogonal states A and B. (For it can then be shown to hold for an adjacent pair of points A and B, from continuity arguments, and hence for *any* pair of states A and B.) As a particular case which proves the general rule, we may see in Fig. 3 that if the *linear* vibration A has a positive advance of phase over the *linear* vibration B, the resultant vibration will be left-elliptic. The results of the discussion of this

paragraph can also be summarised by using the sign convention that the area E′ of the triangle C′BA be counted positive only when the sequence of points C′BA are described in a counter-clockwise sense on the surface of the sphere. We can then write

$$\delta = \pi - \tfrac{1}{2}\mathrm{E}' \qquad (5\,b)$$

§ 5. The Composition of Non-Orthogonally Polarised Pencils

When two coherent beams of intensities I_1 and I_2 (in the states of polarisation A and B respectively) are combined, the resultant state of polarisation C may be specified by the angular distances b and a of the point C from the points A and B (*see* Fig. 2). According to (3) these are given by

$$\sin^2 \tfrac{1}{2}a = \frac{\mathrm{I}_1}{\mathrm{I}} \cdot \sin^2 \tfrac{1}{2}c; \qquad \sin^2 \tfrac{1}{2}b = \frac{\mathrm{I}_2}{\mathrm{I}} \cdot \sin^2 \tfrac{1}{2}c \qquad (6)$$

where I is the resultant intensity given by (1). On proceeding from A to B the point C appears to the left or right according as δ is positive or negative. An alternative method of finding the state C will be given in Part II.

The following geometrical facts are useful for qualitatively locating the state C. When the phase difference between the two beams is altered without altering the ratio of their intensities, the state C moves along the locus $\sin^2 \tfrac{1}{2}a/\sin^2 \tfrac{1}{2}b = \text{constant}$; this is a small circle (with its centre on the great circle through AB) which cuts the arc AB internally and externally according to this ratio (*see* M'Clelland and Preston, *loc. cit.*, Part I, Ch. III, p. 66, Ex. 1). On the other hand, when the ratio of the intensities of the beams is altered without altering their phase difference, the state C moves along the locus, $\mathrm{E}' = \text{constant}$; this is a small circle passing through A and B with its centre on the great circle which is the perpendicular bisector of the arc AB (M'Clelland and Preston, *loc. cit.*, Part II, § 101). The point C is thus determined by the intersection of these two families of small circles.

§ 6. The Composition of Two Oppositely Polarised Beams

When a polarised beam is split into two orthogonally polarised components, A and A′, the fundamental property of the Poincaré sphere enunciated in § 2, I, gives us information regarding the intensities of these components but tells us nothing about their relative phase relationship. When we wish to enquire into the latter, we run into the apparent difficulty that the state of relative phase between the two beams which could be taken as the standard or ' zero ' with respect to which any additional phase differences could be measured, cannot be defined as in § 3 by their interference properties—because there is no such interference to talk of. We can however avoid the difficulty

by restricting ourselves to the following query which alone is of practical importance (*see* Fig. 1).

If, after decomposing a beam of polarisation C_0 into two oppositely polarised beams of polarisation A and A′ respectively, we retard the phase of the A′-component by an amount Δ (relative to the other), and also alter their intensities in any specified manner, what will be the resultant state of polarisation C?

To find the distance of C from A (*see* Fig. 1) constitutes no problem; for, from the first theorem (§ 2, I) itself we see that *the ratio of the* (final) *intensities of the A′ and A beams must be equal to* $\tan^2 \frac{1}{2}CA$. Our question therefore really concerns the magnitude of the angle CAC_0—regarding which we shall prove the following proposition.

VI. The angle CAC_0 is equal to the phase retardation Δ introduced.

It is remarkable that this second important property of oppositely polarised vibrations follows in the ultimate analysis as a consequence of the first fundamental property itself—for we shall prove it is a limiting case of the properties of two non-orthogonally polarised vibrations as they tend towards states of opposite polarisation.

For convenience let us regard the initial and final states of polarisation C_0 and C as given (*see* Fig. 2). We first decompose the beam of polarisation C_0 into two beams of polarisation A and B respectively, where B is chosen such that the arc AB contains C_0. By introducing a phase retardation δ between these beams of polarisation A and B, altering their relative intensities suitably and then compounding them, we can produce a beam of polarisation C. According to § 4, V, we have $\delta = \pi - \frac{1}{2}E'$, where E′ is the area of the triangle C′BA. We wish to find the limit towards which δ tends, as the state of polarisation B tends towards the state A′ opposite to A. As the point B moves towards A′ and ultimately coalesces with it, the area of the triangle C′BA obviously becomes equal to the area of the *lune* enclosed between the great circular arc AC_0A' and AC′A′, this area being $2\angle C_0 AC'$. Hence we have

$$\Delta = \pi - \angle C_0AC' = C\hat{A}C_0$$

thus proving the required proposition. It is clear from (5 *b*) that the angle CAC_0 must be measured positive in the counter-clockwise sense as indicated in Fig. 1, in order that it may have the same sign as Δ (which is the amount by which the A-component is *advanced* in phase).

The particular property of the Poincaré sphere which has led to its extensive application in tracing the passage of polarised light through transparent

birefringent media follows as a corollary of Theorem VI above. On passage through any plate of such a medium, the emergent state of polarisation C can be obtained from the incident state C_0 by a *rotation* of the sphere by an anticlockwise angle Δ about the axis AA′, where A represents the state of elliptic polarisation of the faster of the two orthogonally polarised waves. (The author has not come across a general proof of this much-used property of the Poincaré sphere in any of the references quoted.)

A second corollary of the proposition VI is the following; when the ratio of the intensities of the orthogonally polarised beams is altered without altering their phase relationship, the locus of the resultant state of polarisation C is the great circular arc ACA′.

§ 7. Definition of the 'Phase Difference' Between Oppositely Polarised Vibrations

It will be a great convenience in connection with a later discussion to set up an arbitrary standard with respect to which the relative phase relationship between two orthogonal vibrations may be measured.

When two orthogonal linear vibrations of equal intensity combine to yield a linear vibration bisecting the right angle included between the directions OX and OX′ of their vibrations, we customarily say that the linear vibrations are in phase. (There will be no ambiguity regarding whether the vibrations are to be regarded in phase or opposed in phase, if we choose both the radii vectors OX and OX′ within the interval, $\pi/2 \geqslant \theta > -\pi/2$, with respect to a fixed radius vector Or on the wave-front.)

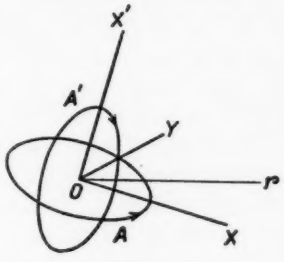

Fig. 4

In conformity with this, we may define two orthogonal elliptic vibrations of equal intensity as being in the same phase when they combine to yield a linear vibration OY bisecting the right angle included between the directions OX and OX′ of their major axes (*see* Fig. 4). The radii vectors OX and OX′ are taken parallel to the major axes of the left- and right-elliptic

vibrations respectively and are chosen such that OXX′Z forms a right-handed system—OZ being the direction of propagation. In terms of the Poincaré representation (*see* Fig. 1), the above definition has the following significance. The states of polarisation of two oppositely polarised vibrations are represented by the points A and A′ on the upper and lower hemisphere respectively, while the linear vibration OY is represented by a point Y. The point Y is one of the two opposite points on the equator at an angular distance of $\pi/2$ from both A and A′; on proceeding from A to Y the upper pole appears to the left, as indicated in the figure. The A- and A′-components of the vibration Y (and hence of any vibration represented by a point on the great circular arc AYA′) are defined to be in the same phase.

The case of opposite circular vibration is not covered in the above definition. We may define two such vibrations of equal intensity to be in the same phase when they yield a linear vibration OY parallel to a fixed radius vector Or on the wave-front.

The phase advance of one polarised vibration A over an orthogonally polarised vibration A′ is then equal to the angle CAY (measured positive in the counter-clockwise sense), where C represents the resultant state of vibration obtained on compounding the two. Henceforward we may speak of any one polarised beam as having a definite phase advance δ over another coherent polarised beam without implying that the two beams are non-orthogonally polarised.

§ 8. INTERFERENCE OF THE COMPONENTS OF TWO POLARISED BEAMS TRANSMITTED BY AN ANALYSER

It is well known that light of any arbitrary elliptic polarisation C′ may be extinguished by means of an appliance consisting of a suitably oriented quarter-wave plate followed by a linear analyser at the proper setting; when light of the opposite polarisation C is incident on the same appliance the *intensity* of the transmitted light will be equal to that of the incident—as may be directly shown (Stokes, 1901), without using any property of the Poincaré sphere. Any appliance having both the above properties will be referred to as an *analyser C*.

Since light of any other polarisation P may be decomposed into two coherent beams of polarisation C and C′, the intensity transmitted by an analyser C will be equal to the C-component of the incident beam. If we assume the fundamental Theorem I, § 2, it follows that an analyser C transmits a fraction $\cos^2 \frac{1}{2}PC$ of the intensity of light of polarisation P. Conversely, one of the simplest proofs of the fundamental Theorem I, lies in the direct analytical

proofs of this property of an analyser given by Fano (1949) and also by Ramachandran and Ramaseshan (1952).

As was pointed out in the Introduction, the problem to be now discussed arises when we wish to consider the phenomena exhibited by a plate of an absorbing biaxial crystal when kept between a polariser and an analyser. Emerging from the crystal plate along any particular direction will be a coherent mixture of two beams 1 and 2. Let their states of polarisation be A and B, their intensities I_1 and I_2, and let the phase advance of the first beam over the second be δ. (The state of polarisation of the resultant beam will not be required here and will *not* be denoted by C.)

In order to compute the intensity transmitted by an analyser C, we first resolve each of the two vibrations into the opposite states of polarisation C and C′ (*see* Fig. 2). The C-components of the beams of polarisation A and B will have intensities $I_1 \cos^2 \frac{1}{2}b$ and $I_2 \cos^2 \frac{1}{2}a$ respectively (§ 2, I). Since these components will have some definite phase difference δ', say, they can interfere. Hence the resultant beam obtained by combining the beams 1 and 2 will have a C-component whose intensity I_C is given by

$$I_C = I_1 \cos^2 \tfrac{1}{2}b + I_2 \cos^2 \tfrac{1}{2}a + 2\sqrt{I_1 I_2} \cos \tfrac{1}{2}a \cos \tfrac{1}{2}b \cos \delta' \quad (7)$$

Similarly the C′-components of the beams 1 and 2 will have intensities $I_1 \sin^2 \frac{1}{2}b$ and $I_2 \sin^2 \frac{1}{2}a$ respectively, and a definite phase difference δ'', say. Hence the C′-component of the resultant beam will have an intensity $I_{C'}$, given by

$$I_{C'} = I_1 \sin^2 \tfrac{1}{2}b + I_2 \sin^2 \tfrac{1}{2}a + 2\sqrt{I_1 I_2} \sin \tfrac{1}{2}a \sin \tfrac{1}{2}b \cos \delta'' \quad (8)$$

Since an analyser transmits only the intensity I_C it remains to determine δ' in terms of the phase difference between the beams 1 and 2, and the analyser position C.

Now δ' represents the phase advance of the C-component of the beam of polarisation A over the C-component of the beam of polarisation B; while δ'' is the phase advance of the C′-component of the beam of polarisation A over the C′-component of the beam of polarisation B. Hence *it follows from a consideration of VI*, § 6, *that* $\delta'' - \delta' = \pm \hat{C}$ (where the positive sign has to be taken if C lies on the side of AB shown in Fig. 2). Furthermore, the intensity I of the resultant beam obtained on compounding 1 and 2 is equal to the sum of the intensities of the C- and C′-components (§ 2, II). Hence adding (7) and (8)

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\{\cos \tfrac{1}{2}a \cos \tfrac{1}{2}b \cos \delta' + \sin \tfrac{1}{2}a \sin \tfrac{1}{2}b \cos (\delta' \pm C)\}$$

Expanding $\cos(\delta' \pm C)$, it can be shown by applying the standard expressions for the spherical excess of a triangle (M'Clelland and Preston, *loc. cit.*, Part II, p. 37, Art. 104) that the above relation reduces to

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\tfrac{1}{2}c\cos(\delta' + \tfrac{1}{2}E)$$

where E represents the area of the triangle ABC itself (counted positive or negative according as the sequence of points A, B, C describe the periphery of the triangle in the counter-clockwise or clockwise sense). The intensity I is also given directly in terms of the phase difference δ between the beams 1 and 2 by the expression (1) of § 3. Comparing the two we get the value of δ' to be substituted in (7):

$$\delta' = \delta - \tfrac{1}{2}E \tag{9}$$

VII. Hence when a mixture of two coherent beams of intensities I_1 and I_2 in the states of polarisation A and B respectively, is incident on an analyser C, the transmitted intensity I_C is given by

$$I_C = I_1\cos^2\tfrac{1}{2}b + I_2\cos^2\tfrac{1}{2}a + 2\sqrt{I_1 I_2}\cos\tfrac{1}{2}a\cos\tfrac{1}{2}b\cos(\delta - \tfrac{1}{2}E) \tag{10}$$

where δ is the phase advance of the beam of polarisation A over the other, a, b and c being the angular sparations BC, CA and AB respectively and E the area of the triangle ABC.

It is to be noted that the above result must also hold in the limiting case when the two beams incident on the analyser are in the orthogonal states of polarisation A and A'. In this case, if AYA' be the great circular arc (Fig. 1) with respect to which the phase difference δ is measured (ref. § 7), then E (which now becomes the area of the lune AYA'CA) is equal to twice the angle CAY. The expression (9) may in this case be further simplified by the substitution $\cos\tfrac{1}{2}a = \sin\tfrac{1}{2}b$.

§ 9. THE ADDITION OF n COHERENT BEAMS

Suppose a mixture of 3 coherent beams of polarisation A_1, A_2, A_3 is incident on an analyser C. Let $2\theta_i$ denote the length of the arc CA_i, δ_{ij} denote the phase *lag* of the beam i over the beam j, and E_{ij} be the area of the triangle A_iCA_j. We have obviously

$$\delta_{ij} = -\delta_{ji}; \qquad E_{ij} = -E_{ji} \tag{11}$$

The C-component of the first vibration may be written as $\sqrt{I_1}\cos\theta_1\,\mathbf{c}\,e^{i\omega t}$ where $\mathbf{c}\,e^{i\omega t}$ is a vibration of unit intensity in the state of polarisation C†.

† The components of the vector c are the complex amplitudes of the components of the elliptic vibration.

If $A\,c\,e^{i\omega t}$ denote the C-component of the resultant vibration obtained on compounding the three vibrations, then according to (9) we will have,

$$A = \sqrt{I_1}\cos\theta_1 + \sqrt{I_2}\cos\theta_2 \exp i(\delta_{12} - \tfrac{1}{2}E_{12}) + \sqrt{I_3}\cos\theta_3 \exp i(\delta_{13} - \tfrac{1}{2}E_{13})$$

Since the phase lag of the C-component of the second beam over the C-component of the third is according to (8), given by $(\delta_{23} - \frac{1}{2}E_{23})$ we have

$$-(\delta_{23} - \tfrac{1}{2}E_{23}) = (\delta_{12} - \tfrac{1}{2}E_{12}) - (\delta_{13} - \tfrac{1}{2}E_{13}) \qquad (12)$$

with similar expressions connecting all the δ_{ij}. Hence the intensity I_C transmitted by an analyser C being equal to AA^*, will be given by

$$I_C = \Sigma I_i \cos^2\theta_i + \sum_{i\neq j} \sqrt{I_i I_j}\cos\theta_i \cos\theta_j \cos(\delta_{ij} - \tfrac{1}{2}E_{ij}) \qquad (13)$$

The resultant intensity I of the beam obtained on compounding the three beams will be equal to the sum of the intensities I_C and $I_{C'}$, where $I_{C'}$ is the intensity transmitted by the orthogonal analyser C′. The resultant intensity can in this manner be shown to be given by

$$I = \Sigma I_i + \sum_{i\neq j} \sqrt{I_i I_j}\cos\tfrac{1}{2}c_{ij}\cos\delta_{ij} \qquad (14)$$

It is obvious that the same argument holds when there are a mixture of n coherent beams; the formula (13) gives the intensity transmitted by an analyser C, while (14) gives the resultant intensity. The state of polarisation of the resultant beam will be deduced incidentally in Part II. We may here merely note that by deducing the intensity transmitted by any analyser C we have a method of deducing the resultant polarisation of the beam: for example, we could find the particular analyser for which the transmitted intensity is zero.

In conclusion the author wishes to express his deep sense of indebtedness to Professor Sir C. V. Raman, F.R.S., N.L., without whose encouragement this work could not have been written.

§ 10. Summary

The superposition of two coherent beams in different states of elliptic polarisation is discussed in a general manner. If A and B represent the states of polarisation of the given beams on the Poincaré sphere, and C that of the resultant beam, the result is simply expressed in terms of the sides, a, b, c of the spherical triangle ABC. The intensity I of the resultant beam is given by:

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\tfrac{1}{2}c\cos\delta;$$

the extent of mutual interference thus varies from a maximum for identically polarised beams ($c = 0$), to zero for oppositely polarised beams ($c = \pi$). The state of polarisation C of the resultant beam is located by $\sin^2 \frac{1}{2}a = (I_1/I) \sin^2 \frac{1}{2}c$ and $\sin^2 \frac{1}{2}b = (I_2/I) \sin^2 \frac{1}{2}c$. The 'phase difference' δ is equal to the supplement of half the area of the triangle C'BA (where C' is the point diametrically opposite to C). These results also apply to the converse problem of the decomposition of a polarised beam into two others.

The interference of two coherent beams after resolution into the same state of elliptic polarisation by an elliptic analyser or compensator is discussed; as also the interference (direct, *and* after resolution by an analyser) of n coherent pencils in different states of polarisation.

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A NEW APPROACH TO THE CASCADE THEORY

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Abstract

The cascade theory of cosmic rays is investigated from a new point of view; we deal with the number of particles produced in a certain thickness of matter, the energy of each particle being greater than E at the point of its production. This new approach leads to an elegant asymptotic theory for large thicknesses and it is better adapted to the interpretation of experiments in nuclear emulsions.

1. Introduction

The cascade theory of cosmic ray showers deals with the number of particles at a given depth t assuming the shower to be initiated by a particle at $t = 0$. In the stochastic problem of cosmic radiation the object was to obtain the probability distribution of this number taking into account the energies of the particles. Defining

$$\pi^i (n_1, n_2, \ldots, n_m;\ E_1, E_2 \ldots, E_m|E_0;\ t)$$

as the probability that there exists n_j particles of type j each of which has an energy greater than E_j ($j = 1, 2, \ldots m$) at t if a cascade is initiated by a particle of type i having an energy E_0, the standard stochastic approach consisted in writing either integral equations for π (integral with respect to t) using the method of regeneration points or the forward differential equations for what are known as the product density functions* at t relating to the particles. Such a treatment of the cascade theory follows the traditional procedure adopted in stochastic processes which evolve with a certain parameter, as for example t, the thickness of matter traversed by a particle. This procedure was natural since cascades were first observed in cloud chambers where the experimental technique was such that it was easy to record particles at a particular thickness. Recently, however, the cascades were observed in nuclear emulsions and Fay at Gottingen pointed out that it was more convenient to estimate the energies of particles at the time of their production rather than of all the particles at any particular thickness. The latter would involve tracing of tracks of the particles which, besides being cumbersome,

* The density functions are related to the moments obtained from π. For the formulation of product densities, *see* Alladi Ramakrishnan, 1950.

introduces large errors in energy measurements. Fay's observations suggest a new mode of approach to the cascade theory.

Instead of defining a π function as before, we define $\Pi^i(n_1, n_2, \ldots, n_m; E_1, E_2, \ldots, E_m | E_0; t)$† as the probability that n_j particles of type j each with energy greater than E_j *at the time of its production* (hereinafter called the primitive energy) are produced between *0 and t*. We shall show that this function in some cases has more elegant mathematical properties than π; and is more suitable for the study of cascades in nuclear emulsions and probably in the bubble chamber where the entire structure of the cascades is expected to be available for observation between *0* and t. It is clear that as in the case of π, it will be a hopeless task to determine Π exactly but it is worthwhile to consider the moments of n_j from Π. This can be done by using the concept of product densities which has been elaborated by one of us (Ramakrishnan, 1950, 1952) in previous papers. While for the sake of brevity, we will be assuming acquaintance with the general theory of product densities, we shall emphasise its adaptation to the problem in detail.

2. The Product Density Functions in the New Approach

We define $F_k(E_1, E_2, \ldots, E_k; t_1, t_2, \ldots, t_k)\, dE_1\, dE_2 \ldots dE_k.\ dt_1\, dt_2 \ldots dt_k$ as the joint probability that an electron of energy between E_1 and $E_1 + dE_1$ is produced between t_1 and $t_1 + dt_1$, an electron of energy between E_2 and $E_2 + dE_2$ is produced between t_2 and $t_2 + dt_2$, ... and an electron of energy between E_k and $E_k + dE_k$ is produced between t_k and $t_k + dt_k$. $F_k(E_1, E_2, \ldots, E_k; t_1, t_2 \ldots, t_k)$ is called the product density of degree k of electrons. We can similarly define $G_k(E_1, E_2, \ldots, E_k; t_1, t_2, \ldots, t_k)$ the product density of degree k of photons and $FG_{l,k-l}(E_1, E_2, \ldots, E_l, E_{l+1} E_{l+2} \ldots, E_k; t_1\ t_2, \ldots, t_k)$ the mixed product density of electrons and photons. Here the l electrons with their energies lying in the intervals $(E_1, E_1 + dE_1)$, $(E_2, E_2 + dE_2)$, ..., $(E_l, E_l + dE_l)$ are produced between t_1 and $t_1 + dt_1$, t_2 and $t_2 + dt_2$, ..., t_l and $t_l + dt_l$ respectively and the $k - l$ photons with their energies lying in the intervals $(E_{l+1}, E_{l+1} + dE_{l+1})$, $(E_{l+2}, E_{l+2} + dE_{l+2}) \ldots, (E_k, E_k + dE_k)$ are produced between t_{l+1} and $t_{l+1} + dt_{l+1}$, t_{l+2} and $t_{l+2} + dt_{l+2}, \ldots, t_k$ and $t_k + dt_k$ respectively.

We note that F_k, G_k and $FG_{l,k-l}$ are product densities over the E- as well as t-space. The properties of such product densities have been established in great detail by one of us (Ramakrishnan, 1954). Using these properties, we see that if the product densities are integrated over $E_1, E_2, \ldots E_k$ over the range E_c to ∞, they are still product densities of particles produced

† Throughout this paper, capital symbols will be used for the corresponding probability and product density functions in the new approach.

between t_i and $t_i + dt_i$ ($i = 1, 2, \ldots k$) the primitive energy of each particle being greater than E_c. Once this product density is obtained, we can obtain the moments by integration over the proper range of t. For example, if we are interested in the r-th moment of the number of electrons produced between 0 and t, the primitive energy of each of the electrons being greater than E_c, it is given by

$$\epsilon\{n^r(E_c; t)\} = \sum_i C_i^r \int_{E_c}^{\infty} dE_1 \int_{E_c}^{\infty} dE_2 \ldots \int_{E_c}^{\infty} dE_i \int_0^t dt_1 \int_0^t dt_2 \ldots \int_0^t dt_i F_i(E_1, E_2, \ldots, E_i; t_1, t_2, \ldots, t_i) \quad (1)$$

where C_i^r are defined in a previous paper (Ramakrishnan, 1950).

At first sight, it may seem that the cascade theory can be built up in terms of the new density functions, without recourse to the old product densities. On the contrary, we find it easier to obtain the integro-differential equations for these functions only by introducing the old density functions. The merit of the new approach lies not so much in giving up the old one but in being a useful adjunct which gives additional information on the cascade. In the next section, we shall obtain integral equations expressing F_k's and G_k's in terms of the old product densities f_k's and g_k's. We shall confine our attention to the first two moments of the number of electrons and photons since explicit solutions of f_k and g_k have not been obtained for $k>2$.

3. Equations Satisfied by the New Product Densities

As is customary we shall assume that the probability per unit thickness of matter that

(1) An electron of energy E radiates a quantum and drops to an energy lying between E′ and E′ + dE' is $R(E'|E)\,dE'$.

(2) A photon of energy E splits up into a pair of electrons one of which has an energy between E′ and E′ + dE' is $\rho(E'|E)\,dE'$. For complete screening, R and ρ, according to Bethe and Heitler (1934), are given by

$$R(E'|E) = \left\{\frac{E - E'}{E} - \left(\frac{4}{3} + a\right)\left(1 - \frac{E}{E - E'}\right)\right\}\frac{1}{E} \quad (2)$$

$$\rho(E'|E) = \left\{1 - \left(\frac{4}{3} + a\right)\left(\frac{E'}{E} - \frac{E'^2}{E^2}\right)\right\}\frac{1}{E} \quad (3)$$

We shall assume only these two processes in the development of the cascade to write the equations based on the new approach. If we take ionisation loss into account corresponding equations can be written down but

our object here is only to suggest the new approach and emphasise its advantage over the old one.

As it will be obvious from what follows that the specification of the initial conditions plays a dominant role in writing down the equations satisfied by F's and G's, we shall use the superscript 1 or 2 according as an electron or a photon of energy E_0 is incident at $t = 0$.

Product Densities of Degree One.—

$F_1^i(E|E_0;\ t)$ and $G_1^i(E|E_0;\ t)$ satisfy the equations

$$F_1^i(E|E_0;\ t) = 2\int_E^{E_0} g_1^i(E'|E_0;\ t)\,\rho(E|E')\,dE' \tag{4}$$

$$G_1^i(E|E_0;\ t) = \int_E^{E_0} f_1^i(E'|E_0;\ t)\,R(E' - E|E')\,dE' \tag{5}$$

where g_1^i and f_1^i are the old product densities of degree one of photons and electrons respectively, *i.e.*, $g_1^i(E|E_0;\ t)\,dE$ represents the probability that a photon lies in the interval $(E, E + dE)$ and $f_1^i(E|E_0;\ t)\,dE$, the probability that an electron lies in $(E, E + dE)$. These according to the theory of product densities represent the mean numbers in the range dE.

(4) and (5) are obtained by arguing that an electron (or a photon) of energy E' $(E' > E)$ should exist at t and must radiate a photon (or produce a pair) between t and $t + dt$. The factor 2 occurs in the R.H.S. of (4) since we do not distinguish between electrons and positrons. These equations are amenable to the usual Mellin transform technique. Defining

$P_1^i(s|E_0;\ t)$ and $Q_1^i(s|E_0;\ t)$ as

$$P_1^i(s|E_0;\ t) = \int_0^\infty F_1^i(E|E_0;\ t)\,E^{s-1}\,dE \tag{6}$$

$$Q_1^i(s|E_0;\ t) = \int_0^\infty G_1^i(E|E_0;\ t)\,E^{s-1}\,dE \tag{7}$$

we obtain

$$P_1^i(s|E_0;\ t) = \gamma_1^i(s|E_0;\ t)\,B_s \tag{8}$$

$$Q_1^i(s|E_0;\ t) = \nu_1^i(s|E_0;\ t)\,C_s \tag{9}$$

where $\nu_1^i(s|E_0;\ t)$ and $\gamma_1^i(s|E_0;\ t)$ are the Mellin transforms of $f_1^i(E|E_0;\ t)$ and $g_1^i(E|E_0;\ t)$ respectively and B_s and C_s are given by

$$B_s \equiv 2\int_0^1 \left[1 - \left(\frac{4}{3} + a\right)(\epsilon - \epsilon^2)\right]\epsilon^{s-1}\,d\epsilon$$

$$= 2\left[\frac{1}{s} - \left(\frac{4}{3} + a\right)\frac{1}{(s+1)(s+2)}\right] \tag{10}$$

$$C_s \equiv \int_0^1 \left[1 - \left(\frac{4}{3} + \alpha\right)\left(\frac{1}{\epsilon} - \frac{1}{\epsilon^2}\right)\right] \epsilon^s \, d\epsilon$$

$$= \frac{1}{s+1} + \left(\frac{4}{3} + \alpha\right) \frac{1}{s(s-1)} \tag{11}$$

Product Densities of Degree 2.—

If $f_2^i(E_1, E_2|E_0;\ t)$, $g_2^i(E_1, E_2|E_0;\ t)$ represent the product densities of degree 2 of electrons and photons respectively and $fg^i{}_{1,1}(E_1, E_2|E_0;\ t)$, the mixed product density of electrons and photons we shall show that assuming $t_2 > t_1$, $F_2^i(E_1, E_2|E_0;\ t_1, t_2)$ satsfies the equation‡

$$\begin{aligned} F_2^i(E_1, E_2|E_0;\ t_1, t_2) &= \int_{E_1}^{E_0} g_1^i(E'|E_0;\ t_1) \cdot 2\rho(E_1|E') \cdot [F_1^1(E_2|E_1;\ t_2 - t_1) \\ &\quad \times H(E_1 - E_2) + F_1^1(E_2|E' - E_1;\ t_2 - t_1) \\ &\quad H(E' - E_1 - E_2)]\, dE' \\ &\quad + \int_{E_2}^{E_0} dE'' \int_{E_2}^{E_0} dE'\, fg^i{}_{1,1}(E', E''|E_0;\ t_1) \cdot 2\rho(E_1|E'') \\ &\quad \times F_1^1(E_2|E';\ t_2 - t_1) \\ &\quad + \int_{E_2}^{E_0} dE'' \int_{E_1}^{E_0} dE' g_2^i(E', E''|E_0;\ t_1)_2\, \rho(E_1|E') \\ &\quad \times F_1^2(E_2|E'';\ t_2 - t_1) \end{aligned} \tag{12}$$

where $H(x)$ is the Heaviside unit function defined as

$$\begin{aligned} H(x) &= 1 && x > 0 \\ &= 0 && \text{otherwise} \end{aligned} \tag{13}$$

(12) is obtained by the following analysis of events.

We shall first define the terms ' ancestor ' and ' parent'. A particle A is the ancestor at t_1 of another particle B created at t_2 $(t_2 > t_1)$ if for the production of the particle B, we need consider the shower produced by A. A particle A at t is the parent of another particle B, if the particle B is produced

‡ For the definition of F_2^i, G_2^i and $FG^i{}_{11}$, it is not necessary to assume that $t_2 > t_1$. However equations satisfied by them can be written down only if we make such an assumption. In integrating them with respect to t_1 and t_2 we must split the integral into two parts: (1) when $t_2 > t_1$; (2) when $t_1 > t_2$. Note also that these functions are not symmetrical in E_1 and E_2 since in assuming $t_2 > t_1$, the order of production is specified.

directly by A. Of course the parent of a particle is an ancestor and obviously the converse does not hold good. The primitive ancestor is the particle that is incident at $t = 0$.

For the derivation of the equation (12), the events can be classified into the following two mutually exclusive sets.

(i) The two electrons, one produced between t_1 and $t_1 + dt_1$ and the other between t_2 and $t_2 + dt_2$ have a common ancestor at t_1.

(ii) The two electrons have two different ancestors at t_1.

The common ancestor at t_1 is the parent of an electron of energy $(E_1, E_1 + dE_1)$ produced between t_1 and $t_1 + dt_1$ and hence is a photon of proper energy; the probability for the existence of a photon of energy E' at t_1 is $g_1^{i}(E'|E_0; t_1)\,dE'$. Thus $2g_1^{i}(E'|E_0; t_1)\,\rho(E_1'|E')\,dE_1dE'dt_1$ represent the probability that a photon of energy between E' and $E' + dE'$ is in existence at t_1 and produces an electron (of energy between E_1 and $E_1 + dE_1$), between t_1 and $t_1 + dt_1$. Since we have assumed that the electron which is produced between t_2 and $t_2 + dt_2$ has the same ancestor as that produced in dt_1, it is equivalent to stating that either the electron of energy E_1 or the other of energy $E' - E_1$ is an ancestor at $t_1 + dt_1$. This is expressed in terms of first order densities and hence we obtain the first term on the R.H.S. of (13).

If we assume that at t_1 we have two different ancestors, since one of the ancestors is the parent between t_1 and $t_1 + dt_1$ of the electron of energy E_1, both of them can be photons or one of them is a photon (this is the parent of the electron produced between t_1 and $t_1 + dt_1$), the other an electron. The probability of this event is expressed by the other two terms.

Using similar arguments for $G_2^{i}(E_1, E_2|E_0; t_1, t_2)$ and $FG^{i}_{1,1}(E_1, E_2|E_0; t_1, t_2)$, we obtain

$$
\begin{aligned}
&G_2^{i}(E_1, E_2|E_0; t_1, t_2) \\
&\quad = \int_{E_1}^{E_0} f_1^{i}(E'|E_0; t_1)\, R(E' - E_1|E')\, \{G_1^{2}(E_2|E_1; t_2 - t_1) \\
&\qquad \times H(E_1 - E_2) + G_1^{1}(E_2|E' - E_1; t_2 - t_1) \\
&\qquad \times H(E' - E_1 - E_2)\}\, dE' \\
&\qquad + \int_{E_1}^{E_0} dE' \int_{E_2}^{E_0} f g^{i}_{1,1}(E', E''|E_0; t_1).\ R(E' - E_1|E') \\
&\qquad \times G_1^{2}(E_2|E''; t_2 - t_1)\, dE'' \\
&\qquad + \int_{E_1}^{E_0} dE' \int_{E_2}^{E_0} f_2^{i}(E', E''|E_0; t_1)\, R(E' - E_1|E') \\
&\qquad \times G_1^{1}(E_2|E''; t_2 - t_1)\, dE''
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
&FG^{i}_{1,1}(E_1, E_2|E_0;\ t_1, t_2)\\
&= \int_{E_1}^{E_0} g_1^{i}(E'|E_1;\ t_1).\ 2\rho(E_1|E')\ \{G_1^{1}(E_2|E_1;\ t_2 - t_1)\\
&\quad \times H(E_1 - E_2) + G_1^{1}(E_2|E' - E_1;\ t_2 - t_1)\\
&\quad \times H(E' - E_1 - E_2)\}\, dE'\\
&\quad + \int_{E_1}^{E_0} dE'' \int_{E_2}^{E_0} f g^{i}_{1,1}(E', E''|E_0;\ t_1) \cdot 2\rho(E_1|E'')\\
&\quad \times G_1^{1}(E_2|E';\ t_2 - t_1)\, dE'\\
&\quad + \int_{E_1}^{E_0} dE'' \int_{E_2}^{E_0} g_2^{i}(E', E''|E_0;\ t_1) \cdot 2\rho(E_1|E'')\\
&\quad \times G_1^{2}(E_2|E';\ t_2 - t_1)\, dE' \qquad (15)
\end{aligned}
$$

This set of equations is however incomplete. Since in (15) we have assumed that $t_2 > t_1$, it also implies that the electron is produced prior to the photon. If the photon is produced prior to the electron, that is, if $t_1 > t_2$, then $FG^{i}_{1,1}$ satisfies an equation different from (15). In (12) and (14), if $t_1 > t_2$, we have merely to interchange t_1, t_2 and E_1, E_2 on the right-hand side of the equations. By arguments, similar to those by which (15) was obtained, we write in the case when $t_1 > t_2$*

$$
\begin{aligned}
&FG^{i}_{1,1}(E_1, E_2|E_0;\ t_1, t_2)\\
&= \int_{E_1}^{E_0} f_1^{i}(E'|E_0;\ t_2)\, R(E' - E_2|E')\, dE'\ \{F_1^{1}(E_1|E';\ t_1 - t_2)\\
&\quad \times H(E' - E_2 - E_1) + F_1^{2}(E_1|E_2;\ t_1 - t_2)\, H(E_2 - E_1)\}\\
&\quad + \int_{E_2}^{E_0} dE' \int_{E_1}^{E_0} dE'' f g^{i}_{1,1}(E', E''|E_0;\ t_2)\, R(E' - E_2|E')\\
&\quad \times F_1^{2}(E_2|E'';\ t_1 - t_2)\\
&\quad + \int_{E_2}^{E_0} dE' \int_{E_1}^{E_0} dE'' f_2^{i}(E', E''|E_0;\ t_2)\, R(E' - E_2|E')\\
&\quad \times F_1^{1}(E_1|E'';\ t_1 - t_2) \qquad (15\,a)
\end{aligned}
$$

* Only in equations (15 *a*) and (21 *a*) is it assumed that $t_1 > t_2$. In all other equations, $t_2 > t_1$. Hence the addition of the letter *a* to the numbers of equations.

To solve equations (13) to (15), we make the double Mellin transformation defined by

$$P_2^i(r, s|E_0;\ t_1, t_2) = \int_0^\infty dE' \int_0^\infty dE_2 F_2^i(E_1, E_2|E_0;\ t_1, t_2)\, E_1^{r-1} E_2^{s-1} \tag{16}$$

$$Q_2^i(r, s|E_0;\ t_1, t_2) = \int_0^\infty dE_1 \int_0^\infty dE_2\, G_2^i(E_1, E_2|E_0;\ t_1, t_2)\, E_1^{r-1} E_2^{s-1} \tag{17}$$

$$PQ^i{}_{1,1}(r, s|E_0;\ t_1, t_2) = \int_0^\infty dE_1 \int_0^\infty dE_2 FG^i{}_{1,1}(E_1, E_2|E_1;\ t_1, t_2)\, E_1^{r-1} E_2^{s-1} \tag{18}$$

If $\nu_2^i(r, s|E_0;\ t)$, $\gamma_2^i(r, s|E_0;\ t)$ and $\nu\gamma^i{}_{1,1}(r, s|E_1;\ t)$ are the Mellin transforms of $f_2^i(E_1, E_2|E_1;\ t)$, $g_2^i(E_1, E_2|E_0;\ t)$ and $fg^i{}_{1,1}(E_0, \Xi_2|E_0;\ t)$ respectively, we obtain the Mellin transform solution of equations (13) to (15) as

$$\begin{aligned} P_2^i(r, s|E_0;\ t_1, t_2) &= \frac{1}{E_0^{s-1}} \{\gamma_1^i(r+s-1|E_0;\ t_1)\, P_1^1(s|E_0;\ t_2 - t_1) \\ &\quad \times [B_{r+s-1} + a_1(r, s)] \\ &\quad + P_1^1(s|E_0;\ t_2 - t_1)\, B_r\, \nu\gamma^i{}_{1,1}(s, r|E_0;\ t_1) \\ &\quad + P_1^2(s|E_0;\ t_2 - t_1)\, B_r\, \gamma_2^i(r, s|E_0;\ t_1)\} \end{aligned} \tag{19}$$

$$\begin{aligned} Q_2^i(r, s|E_0;\ t_1, t_2) &= \frac{1}{E_0^{s-1}} \{\nu_1^i(r+s-1|E_0;\ t_1)\, [C_{r+s-1}\, Q_1^1(s|E_0;\ t_2 - t_1) \\ &\quad + a_2(r, s)\, Q_1^2(s|E_0;\ t_2 - t_1)] \\ &\quad + Q_1^1(s|E_0;\ t_2 - t_1)\, C_r\, \nu\gamma^i{}_{1,1}(r, s|E_0;\ t_1) \\ &\quad + Q_1^2(s|E_0;\ t_2 - t_1)\, C_r\, \nu_2^i(r, s|E_0;\ t_1)\} \end{aligned} \tag{20}$$

$$\begin{aligned} PQ^i{}_{1,1}(r, s|E_0;\ t_1, t_2) &= \frac{1}{E_0^{s-1}} \{\gamma_1^i(r+s-1|E_0;\ t_1)\, Q_1^1(s|E_0;\ t_2 - t_1) \\ &\quad \times [B_{r+s-1} + a_1(r, s)] \\ &\quad + Q_1^2(s|E_0;\ t_2 - t_1)\, B_r\, \nu\gamma^i{}_{1,1}(s, r|E_0;\ t_1) \\ &\quad + Q_1^1(s|E_0;\ t_2 - t_1)\, B_r\, \gamma_2^i(r, s|E_0;\ t_1)\} \end{aligned} \tag{21}$$

$$PQ^{i}_{1,1}(r, s|E_0;\ t_1, t_2)\ (\text{if } t_1 > t_2)$$

$$= \frac{1}{E_0^{r-1}}\{\nu_1^{i}(r+s-1|E_0;\ t_2)\,[P_1^{1}(r|E_0;\ t_1-t_2)\,a_2(s, r) + P_1^{2}(r|E_0;\ t_1-t_2)\,C_{r+s-1}] + \nu\gamma^{i}_{1,1}(s, r|E_0;\ t_2)\,C_s\,P_1^{2}(r|E_0;\ t_1-t_2) + \nu_2^{i}(r, s|E_0;\ t_2)\,C_s\,P_1^{1}(r|E_0;\ t_1-t_2)\} \qquad (21\,a)$$

$a_1(r, s)$ and $a_2(r, s)$ are defined by

$$a_1(r, s) = \frac{2\,|\overline{(r)}\ |\overline{(s)}}{|\overline{(r+s)}}\left\{1-\left(\frac{4}{3}+\alpha\right)\frac{rs}{(r+s)(r+s+1)}\right\}$$

$$a_2(r, s) = \frac{|\overline{(r)}\ |\overline{(s)}}{|\overline{(r+s)}}\left\{\frac{s}{r+s}+\left(\frac{4}{3}+\alpha\right)\frac{r}{s-1}\right\} \qquad (22)$$

In obtaining the equations (19) to (21) we have assumed that $P_1^{i}(s|E_0;\ t)|E_0^{s-1}$ and $Q_1^{i}(s|E_0;\ t)|E_1^{s-1}$ are independent of E_0. But this can be readily proved using (9), (10) and the properties of $\nu_1^{i}(s|E_0;\ t)$ and $\gamma_1^{i}(s|E_0;\ t)$.

Since ν_2. γ_2 and $\nu\gamma_{1,1}$ have been explicitly solved (*see* Bhabha and Ramakrishnan, 1950) we can obtain F_1^{i}, G_1^{i}, F_2^{i}, G_2^{i} and $FG^{i}_{1,1}$ by inverting the corresponding P^{i} or Q^{i}. If we are interested in the mean square number of electrons produced between 0 and t with their individual primitive energies being greater than E_c, we can use (1) and evaluate the resulting contour integrals by the saddle point method.

4. Asymptotic Behaviour of Cascades for Large Thicknesses

It is well known that the old product densities and all the moments of the number of particles above a certain energy E_c ($E_c > 0$) at thickness t tend to zero as $t \to \infty$. This is obvious from a physical point of view. Since the Bethe-Heitler cross-sections are homogeneous the total cross-section is independent of the energy of the particle and as such the probability of finding a particle above a certain energy E_c at t tends to zero as $t \to \infty$. As the new product densities are expressed as linear combinations of the old densities we can assert always that for the same reason, the moments of the number of particles that are produced between 0 and t with the primitive energy of each particle being greater than E_c tends to a finite limit as $t \to \infty$. We shall demonstrate the existence of these limits by taking the first order product densities for a shower excited by an electron of energy E_0.

From equations (1), (9) and (10), the mean numbers of electrons and photons produced between 0 and t, the primitive energy of each of them being $> E_c$ are given by

$$\epsilon\{N(E_c|E_0;\ t)\} = \frac{1}{2\Pi i}\int_0^t d\tau \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{B_s \gamma_1^1(s|E_0;\ \tau)}{s-1}\left(\frac{E_0}{E_c}\right)^{s-1} ds \tag{23}$$

$$\epsilon\{M(E_c|E_0;\ t)\} = \frac{1}{2\Pi i}\int_0^t d\tau \int_{\sigma-i\infty}^{\sigma+i\infty} \frac{C_s\ \nu_1^1(s|E_0;\ \tau)}{s-1}\left(\frac{E_0}{E_c}\right)^{s-1} ds \tag{24}$$

Inverting the order of integration over s and τ and using the solutions $\nu_1^1(s|E_0;\ \tau)$ and $\gamma_1^1(s|E_0;\ \tau)$ we obtain

$$\epsilon\{N(E_c|E_0;\ t)\} = \frac{1}{2\Pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{B_s C_s}{(\mu_s-\lambda_s)(s-1)}\left(\frac{E_0}{E_c}\right)^{s-1}\left[\frac{1-e^{-\lambda_s t}}{\lambda_s} - \frac{1-e^{-\mu_s t}}{\mu_s}\right] ds \tag{25}$$

$$\epsilon\{M(E_c|E_0;\ t)\} = \frac{1}{2\Pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{C_s}{(s-1)(\mu_s-\lambda_s)}\left(\frac{E_0}{E_c}\right)^{s-1}\left[\frac{D-\lambda_s}{\lambda_s}(1-e^{-\lambda_s t}) + \frac{\mu_s - D}{\mu_s}(1-e^{-\mu_s t})\right] ds \tag{26}$$

where the λ's and μ's have been defined in earlier papers [*see* for example, Bhabha and Ramakrishnan (1950)].

Expressed in this form it is easy to see that $\epsilon\{N(E_c|E_0;\ t)\}$ and $\epsilon\{M(E_c|E_0;\ t)\}$ tends to a finite limit as $t \to \infty$.

In an exactly similar manner it can be demonstrated from equations (18) to (20) that the second moment of the number of particles produced (above a certain non-zero primitive energy) tends to a finite limit as $t \to \infty$ by using the Mellin transform sloutions for f_2, $fg_{1,1}$ and g_2. This will be done in a later contribution wherein the numerical results pertaining to fluctuations will be presented.

The numerical evaluation of the mean number of electrons produced for various thicknesses and primitive energies forms the subject-matter of a later paper by one of us (S.K.S.) and N. R. Ranganathan.

One of us (R.) expresses his thanks to Professor W. Heisenberg for his kind invitation to visit the Max Planck Institute at Gottingen where this problem was suggested by Mr. Fay on the basis of his experimental results and the other (S.K.S.) is grateful to the University of Madras for the grant of a Government of India Scholarship.

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SCATTERING OF POLARISED LIGHT BY COLLOIDS CONTAINING ANISOTROPIC PARTICLES

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1. Introduction

When a beam of light traverses any colloidal medium a part of it is scattered in all directions. The light scattered in any particular direction is characterised by two parameters namely intensity and state of polarisation. These factors vary with the size, shape and distribution of the particles and with the angle of scattering. If the incident light is plane polarised the scattered light is also plane polarised as long as the particles are spherical and small compared with the wavelength of light. If the particles are small but anisotropic the scattered light will be partially polarised or depolarised but not elliptically polarised. If the particles are of a size comparable with the wavelength of light, the scattering is multipolar in character and in general has an elliptically polarised part. Under such circumstances the depolarisation factor ρ_h for incident light polarised in the horizontal plane has a value less than unity. The finite size of the particle can, therefore, be detected and estimated either by the extent to which ρ_h is less than unity or by the existence of ellipticity in the scattered light. Perrin (1939, 1942) showed theoretically that the existence of ellipticity in the scattered light would be a more sure test of the multipolar character of the scattering of light by any colloid.

The experiments carried out by the earlier workers on the ellipticity of the scattered light were not designed to bring out clearly the implications of Mie's theory (1908). Using the Babinet compensator method the light scattered by certain heterogeneous media was shown to be elliptically polarised by Darbara Singh (1942), Hariharan (1942), Krishnan and Venkata Rao (1944) and George (1950). Conclusions of a qualitative nature were drawn by them regarding the size of the scattering particles from the range of angles of polarisation of the incident beam over which they were able to detect any elliptic polarisation in the light scattered in the horizontal transverse direction. It is only recently that the theoretical implications of Mie's theory regarding ellipticity have been clearly brought out by the work of LaMer

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and Kerker (1950), Kastler (1952), Krishnan, Narayanan and Sivarajan (1954). From Mie's theory one can deduce that when the incident light is plane polarised in any azimuth, there exists a phase difference between the vertical and horizontal components of the light transversely scattered by large spherical particles, which is independent of the azimuth of polarisation, α, of the incident beam. This phase difference δ is a function of the size and the relative refractive index of the particles. Krishnan, Narayanan and Sivarajan (1954) recently carried out experiments specially designed to bring out these facts. They gave a satisfactory explanation for the qualitative results of the earlier workers on ellipticity, which showed apparent variation of ellipticity with the angle of polarisation of the incident beam. In the case of identical particles possessing spherical symmetry, δ will be the same for the individual particles of the medium and consequently the scattered light by the medium as a whole will be completely polarised. In the case of non-spherical particles, however, in addition to the polarised scattering arising from the finite size, there will be some depolarised scattering arising from varying orientations of the anisotropic particles. Using the method suggested by Krishnan, Narayanan and Sivarajan (1954) an experimental study has therefore been made on the ellipticity of the transversely scattered light in the case of carefully prepared aqueous colloidal sols containing anisotropic particles and these results are reported in this paper.

2. Experimental

Preparation of the Sols

The following sols which are known to contain anisotropic particles were prepared: Graphite sol, arsenic trisulphide sol, gelatine sol, gold and silver sols. The details of preparation have already been given in the earlier papers of Krishnan (1937). The sols were prepared in dust-free double distilled water and care was taken to ensure the absence of dust from the solutions.

Optical Set-up

Since the object of the experiment was to measure the phase difference δ that existed between the vertical and horizontal components of the scattered light, the Babinet compensator had to be set with its axes vertical and horizontal. Under such conditions, when the incident beam was linearly polarised, the elliptic polarisation in the transversely scattered light would be exhibited in the field of view of the compensator-analyser combination as a shift of the fringes with respect to the crosswire. This shift is a measure of the phase difference δ. If, however, the compensator was set with its axes at 45° to the vertical, one no longer measured the phase difference δ, but some

phase difference of the resolved components along the axes of the compensator which were at 45° to the vertical. One would therefore, observe a continuous shift of the fringes past the crosswire as one varies the azimuth of polarisation α of the incident beam, α being the inclination of the plane of polarisation with respect to the vertical. This procedure was employed by the earlier workers and consequently their qualitative results could not satisfactorily be correlated with the implications of Mie's theory.

Both methods of observation were used in our experiments. The source of light was sunlight reflected by means of a Foucault heliostat into a darkened room through an aperture in one wall. The light was condensed by means of a long focus Dallmeyer lens and rendered nearly parallel with the aid of a second lens. It was then allowed to fall on the rectangular glass cell containing the colloid. Filters were used in the path of the incident beam to give a narrow band of wavelengths. Observations were made in the transverse horizontal direction, suitable precautions being taken to avoid errors due to stray light, etc. By using a Fuess polarising microscope kept with its axis horizontal in conjunction with a Babinet compensator analyser combination, the compensator could be rotated and the position of its axes accurately measured. With the compensator axes set vertical and horizontal, measurements were made of δ for various values of α. The depolarisation factors ρ_u, ρ_v and ρ_h were also measured for the colloids investigated.

3. Results and Discussion

It was found that the phase difference δ was independent of the azimuth of polarisation α, of the incident beam. Variations observed if any in the value of δ were within the limits of experimental error. The average values of the phase difference δ for α from 0–90° for the different colloids were determined and are given in Table I together with the values for the depolarisation factors ρ_u, ρ_v and ρ_h. From the observed values of ρ_v and ρ_h it is evident that we are here dealing with large anisotropic particles ($\rho_v \neq 0$, $\rho_h < 100\%$).

It was also found that in all the cases, when the axes of the ellipse were inclined at 45° to the vertical, the corresponding values of α were such that $\rho_\alpha = 100\%$. The same result was observed with spherical particles also. Thus, an extremely interesting fact emerges from this study, namely that even in the case of large anisotropic particles, the scattered radiation exhibits elliptic polarisation with a constant phase difference between the vertical and horizontal components which is independent of the azimuth of polarisation of the incident beam. This is what is to be expected theoretically in the case of a colloidal medium containing large anisotropic particles which are randomly

TABLE I

Sol	ρ_u%	ρ_v%	ρ_h%	Average value of δ
Graphite	19	6	36	60°
Gelatine	6·8	2·5	57	59°
Arsenic trisulphide ..	33	3·4	11	7·5°
Silver sol A	32	12·3	52	96°
Silver sol B	15	3·0	57	9°
Gold sol	18·4	4·4	82	78°

oriented. Such a scattering medium can be considered as symmetrical. The Stokes parameters of the light transversely scattered by a symmetrical scattering medium are given by the following set of equations which are the same as 47 A in Perrin's (1942) paper.

$$\begin{aligned} I' &= a_1 I + b_1 M \\ M' &= b_1 I + a_2 M \\ C' &= a_3 C + b_2 S \\ S' &= -b_2 C + a_4 S \end{aligned} \qquad (1)$$

The phase difference δ of the scattered light is given by the relation

$$\tan \delta = \frac{S'}{C'} \qquad (2)$$

If the incident light is plane polarised in a direction making an angle α with the perpendicular to the scattering plane, *i.e.*, vertical, $I = 1$, $M = -\cos 2\alpha$, $C = \sin 2\alpha$ and $S = 0$. Substituting these values in (2) and (1) we get

$$\tan \delta = -\frac{b_2}{a_3}$$

It follows therefore, that the phase difference δ for the scattered light is independent of the azimuth of polarisation of the incident beam. This is what has been observed experimentally.

SUMMARY

It is only recently that the theoretical significance of the elliptic polarisation of light scattered by colloids containing particles of large size has been

pointed out and an analysis made of the theoretical conclusions regarding ellipticity from Mie's theory for spherical particles. The earlier qualitative measurements on ellipticity of the scattered light have been explained on the basis of these new ideas and the implications of Mie's theory brought out more clearly. New experiments have been devised and used for measuring the constant phase difference δ that exists between the vertical and horizontal components of the transversely scattered light when the incident light is polarised in any azimuth. Measurements have been made both for systems of spherical particles and anisotropic particles. It is found that even in the case of large anisotropic particles δ is a constant. It follows therefore, that in the most general case of large anisotropic colloidal particles the polarised scattering due to finite size is elliptic in nature and is superposed on the depolarised part due to anisotropy.

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CONSTITUTION OF MAXIMA SUBSTANCE A

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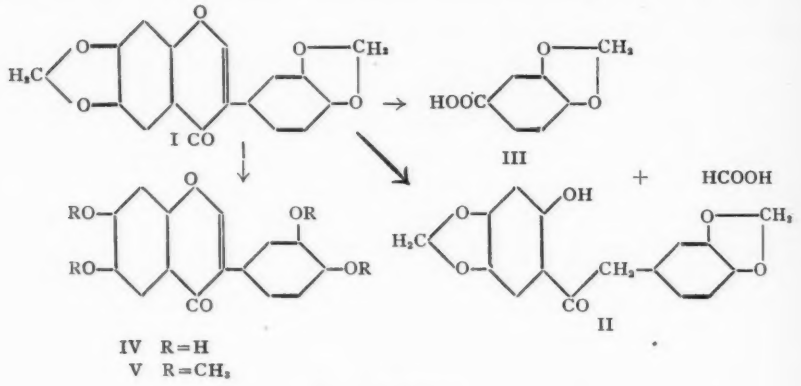
Maxima substance A was isolated from the chloroform extract of the roots of *Tephrosia maxima* Aers.[1] It forms colourless plates from benzene melting at 227–29° and has the probable molecular formula $C_{17}H_{10}O_6$. It did not answer the rotenoid colour reactions and the substance was recovered after treatment with iodine and sodium acetate in boiling alcohol. It was insoluble in aqueous sodium hydroxide and did not give any colour with ferric chloride. It was recovered even after boiling for three hours with acetic anhydride and sodium acetate. It did not form a derivative with 2:4-dinitrophenylhydrazine. It dissolved in concentrated sulphuric acid forming a yellow solution but the substance was recovered on dilution with water. It contained no methoxyls (micro-Zeisel) but gave positive test for the methylenedioxy grouping (green colour with gallic acid and sulphuric acid).

Boiling the substance with 12% alkali gave rise to formic acid and a phenolic ketone (II) melting at 142–44° and having a molecular formula $C_{16}H_{12}O_6$. Formic acid was identified by its reducing action on mercuric chloride and by its reduction to formaldehyde which was again identified by its colour reactions. On oxidation of maxima substance A with alkaline hydrogen peroxide, piperonylic acid (III) was obtained. These reactions suggest for the substance an isoflavone structure with a methylenedioxy group at 3′:4′ position. An isoflavone with a methylenedioxy group at 3′:4′ position should have the molecular formula $C_{16}H_{10}O_4$. Hence Maxima substance A, which has the formula $C_{17}H_{10}O_6$ will be an isoflavone with two methylenedioxy groups. This was confirmed by the fact that treatment of maxima substance A with anhydrous aluminium chloride in boiling benzene solution gave a tetrahydroxy-isoflavone (IV) due to demethylenation. This demethylenation did not go well when hydriodic acid or hydrobromic acid was employed. The tetrahydroxy compound (IV) was characterised by methylating it with dimethyl sulphate and potassium carbonate in acetone solution when it yielded the tetramethyl ether (V). Since there is only one methylenedioxy group in the side phenyl nucleus, the second methylenedioxy group should be located in the benzene ring of the benzo-pyrone part of the molecule. There are three possibilities for the position of this second methylenedioxy group, namely, 5:6, 6:7 or 7:8. An isoflavone with a hydroxyl in position 5 should be sparingly soluble in aqueous alkali and should give a positive

Wilson's boric-citric reaction.[2] Since the tetrahydroxyisoflavone (IV) was easily soluble in aqueous alkali and gave a negative Wilson's boric-citric reaction, the 5:6 position for the second methylenedioxy group in the parent compound seems to be ruled out. The phenolic ketone (II) failed to give a blue colour with 2:6-dichloroquinonechlorimide reagent under the conditions described by Hochberg *et al.*[3] This may mean that in this compound the position *para* to the phenolic hydroxyl is not free. These observations seem to indicate that the second methylenedioxy group in Maxima substance A is probably in the 6:7 position. The 7:8 position for the methylenedioxy grouping does not seem very likely in view of the fact that few 8-hydroxy- or 8-methoxyisoflavones have so far been reported to occur in nature. A rigid proof for the 6:7 position for the methylenedioxy group is very desirable and possibilities in this direction are being explored.



EXPERIMENTAL

Maxima substance A was obtained as colourless crystalline plates, m.p. 227–29° from benzene (Found: C, 66·1, H, 3·7%; OCH_3, Nil. $C_{17}H_{10}O_6$ requires C, 65·8; H, 3·3%).

Hydrolysis of maxima substance A

(*a*) *With alkaline hydrogen peroxide.*—The substance (250 mg.) was dissolved in 25 c.c. of 5% alcoholic potassium hydroxide (made with 80% alcohol) by warming for 15 minutes and 30% hydrogen peroxide was added little by little (total 3 c.c.). When the effervescence ceased, the solution was warmed on a water-bath to decompose the excess of hydrogen peroxide, diluted to 100 c.c., acidified with dilute hydrochloric acid and extracted with ether. The ether extract was divided into acidic, phenolic and neutral fractions by extracting with 5% aqueous sodium bicarbonate and 5% aqueous

sodium hydroxide. The acidic fraction (100 mg.) on two crystallisations from acetone-petroleum ether gave colourless plates melting at 225–28°. It did not give any colour with ferric chloride but gave a green colour with gallic acid and sulphuric acid [Found: C, 58·3; H, 4·1%. $C_8H_6O_4$ (piperonylic acid) requires C, 57·8; H, 3·6%]. The mixed m.p. with an authentic specimen of piperonylic acid melting at 230–32° was 228–30°.

The phenolic fraction (80 mg.) on crystallisation from benzene-petroleum ether gave colourless shining needles, initially melting at 131–32°, again crystallising and remelting at 142–44°. When the substance was dried at 80° for three hours it melted directly at 142–44°. It gave a reddish brown colour with ferric chloride. It formed a greenish yellow solution in concentrated sulphuric acid which turned deep green when warmed with a speck of gallic acid [Found: C, 64·6; H, 4·5%. $C_{16}H_{12}O_6$ (phenolic ketone II) requires C, 64·0; H, 4·0%].

The 2:4-dinitrophenylhydrazone of the phenolic ketone (II) prepared in the usual manner crystallised from chloroform-methanol as bright yellow plates, m.p. 239–41° (Found: C, 55·7; H, 3·7; N, 12·1%. $C_{22}H_{16}O_9N_4$ requires C, 55·0; H, 3·4; N, 11·7%).

(*b*) *With* 12% *sodium hydroxide*.—Maxima substance A (436 mg.) was suspended in a solution of 12% sodium hydroxide made with 50% alcohol (50 c.c.) and refluxed until the whole of the substance went into solution (about 30 minutes), cooled, diluted with 100 c.c. of water, made acidic to congo red with 20% phosphoric acid and cooled in the ice-chest for one hour. The solid (X) that separated was filtered and washed free from acid with water. The filtrate and washings were extracted with petroleum ether (3 × 100 c.c.). The petroleum ether was washed with small quantities of water and these washings and aqueous layer (Y) were reserved for the estimation of formic acid.

The residue from the petroleum ether extract and the solid (X) were mixed, dissolved in ether and washed with 5% aqueous sodium bicarbonate. The ether was evaporated and the residue (300 mg.) was crystallised from methanol. Colourless plates melting at 131–32°, solidifying and remelting at 142–44° were obtained. This substance was identical with the phenolic ketone obtained in experiment (*a*).

Formic acid.—The aqueous liquid (Y) was steam distilled and about 500 c.c. of distillate was collected. The formic acid in the distillate was determined by titration with N/20 sodium hydroxide using phenolphthalein as indicator (yield: 50% of theoretical).

The neutralised distillate was reduced to a small bulk. A portion of it was reduced with magnesium and sulphuric acid (1 : 4) cooling the solution in ice. The resulting solution answered all the qualitative tests for formaldehyde. Another aliquot portion of the neutralised distillate was used for the estimation of formic acid by Riesser's method[4] (reduction of mercuric chloride to mercurous chloride and back oxidation of mercurous chloride to mercuric chloride with standard iodine solution) (yield: 50% of theoretical).

(*c*) *With* 30% *potassium hydroxide*.—Maxima substance A (250 mg.) was boiled with 20 c.c. of 30% alcoholic potash for 3 hours, cooled, diluted with water (100 c.c.), acidified with dilute hydrochloric acid and extracted with ether. The ether extract was divided into acidic, phenolic and neutral fractions as usual. The only crystalline product obtained was the phenolic ketone (II).

Demethylenation of maxima substance A to 6 : 7 : 3′ : 4′-*tetrahydroxyisoflavone*.—Maxima substance A (200 mg.) in benzene (20 c.c.) was treated with anhydrous aluminium chloride (2 g.) and the mixture was boiled under reflux for 2½ hours. The mixture was cooled, the benzene solution was decanted off into another flask and the solvent was removed under vacuum. To the residues in the two flasks 1 : 1 hydrochloric acid was added to decompose the complex and the solution was extracted with ether. The yellow ether solution was extracted with 2% aqueous sodium hydroxide. The alkali-soluble portion was recovered by acidification and extraction with ether. The ether solution was dried and evaporated under vacuum. The residue was taken in the minimum amount of ethyl acetate and benzene was added drop by drop until turbidity developed. On cooling in the ice-chest resins sticking to the sides separated. The mother liquor was decanted into another vessel and the process of adding benzene and removal of resins was repeated thrice. Finally the clear benzene-ethyl acetate solution was concentrated and kept in the ice-chest. The yellow crystalline solid that separated was crystallised again from methanol-benzene. Dark yellow prisms and needles, darkening at about 270° and melting at 320° (decomp.), were obtained. The solution gave a dark green colour with alcoholic ferric chloride. No green colour was obtained on warming with concentrated sulphuric acid and gallic acid. No yellow colour was developed in Wilson's boric-citric reaction. The substance was insoluble in aqueous sodium bicarbonate and completely soluble in aqueous sodium hydroxide forming a yellow solution [Found: C, 62·5; H, 3·5%, $C_{15}H_{10}O_6$ requires C, 63·0; H, 3·5%].

6:7:3′:4′-*tetramethoxyisoflavone*.—The above tetrahydroxyisoflavone (40 mg.) in acetone (10 c.c.), dimethyl sulphate (0·4 c.c.) and anhydrous potassium carbonate (1 g.), were refluxed together on a water-bath for 5 hours. The acetone was decanted off, the potassium carbonate was washed with acetone, the acetone solutions were evaporated under vacuum and the residue was treated with water. The precipitated solid was filtered, washed with 2% aqueous sodium hydroxide and finally free from alkali with water. The substance was dried and purified by two crystallisations from methanol-petroleum ether. Colourless prisms (30 mg.) melting at 168–70° were obtained. The substance did not give any colour with ferric chloride [Found: C, 66·2; H, 5·7; OCH_3, 35·1%. $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3; OCH_3 (4), 36·3%].

Summary

Maxima substance A has been shown to be a dimethylenedioxy-isoflavone. One of the methylenedioxy groups is in the 3′:4′-position of the side phenyl nucleus; the other is most probably in the 6:7 position in the benzopyrone part.

Acknowledgment

We thank Mr. E. Venkata Rao for the microanalyses.

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ISOLATION AND CONSTITUTION OF PATULITRIN

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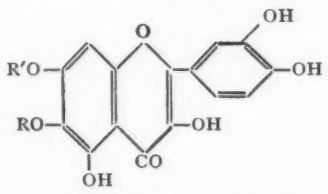
The isolation of patuletin[1] from the flowers of *Tagetes patula* (French marigold) and the establishment of its constitution[2] as 6-methoxy-3 : 5 : 7 : 3′ : 4′-pentahydroxy flavone (I *a*) has already been reported. In the course of this work the presence of a glycoside in small quantities was recorded. Subsequently, from a number of test extractions it was found that the mature flowers, particularly late in the season, contained no glycoside and only early season flowers and especially buds contained appreciable amounts and fresh flowers were the most suitable for extraction. A similar observation has been made with the flowers of *Tagetes erecta* which also yield the glucoside, quercetagitrin (I *b*) only when collected in the early season. Using fresh flush of flowers and buds of *T. patula*, it has now been possible to isolate the glycoside in a crystalline condition. Its solubility and other properties are similar to those of quercetagitrin. On hydrolysis with mineral acid it yields patuletin and one mole of glucose. The position of the sugar unit has been established by complete methylation of the glycoside and hydrolysis of the product yielding 7-hydroxy-3 : 5 : 6 : 3′ : 4′-pentamethoxy flavone,[3] whose identity has been confirmed by ethylation and mixed melting point determination of the methyl-ethyl ether with a synthetic sample.[4] The new glycoside is, therefore, patuletin 7-mono-glucoside (I *c*) and has been named patulitrin.



I *a* R = CH_3; R′ = H
b R = H ; R′ = glucose residue
c R = CH_3; R′ = glucose residue

The occurrence of quercetagetin (nor-patuletin) also as 7-monoglucoside (I *b*) in the closely related plant *T. erecta* would appear to be significant and suggest that the partial methylation of quercetagitrin possibly leads to the formation of patulitrin which eventually produces patuletin by hydrolysis. In an earlier publication by Pankajamani and Seshadri[5] various possible methods leading to the formation of partial methyl ethers of flavonoids in nature were discussed. Protection of reactive hydroxyl groups (*e.g.*, 7-hydroxyl) by glycoside formation was recognised as one of the important

methods involved. In the present case of patulitrin the other hydroxyl groups in 3, 3′ and 4′-positions should have been protected by other mechanisms.

Experimental Procedure

Isolation.—Petals of fresh flowers (5 lb.) were extracted thrice with boiling rectified spirits (3 litres) for 12 hours each time. The combined extract (9 litres) was concentrated under reduced pressure to recover most of the solvent whereby reddish-brown petrol-soluble waxy matter separated out of the aqueous alcoholic concentrate. It was filtered off and the filtrate exhaustively extracted with ether. On standing in the refrigerator for a month, it deposited pale-yellow crystals (1 g.). When crystallised from acetone methanol mixture it came out as pale-yellow needles, m.p. 253–54° (d.). It was soluble in ethyl and methyl alcohols, sparingly soluble in acetone and water and insoluble in ether. It gave an olive brown colour with ferric chloride and reddish pink colour with magnesium and hydrochloric acid and readily dissolved in aqueous sodium hydroxide (1%), carbonate (5%) and borax (5%) yielding bright yellow solutions. Neutral and basic lead acetate solutions precipitated red-coloured lead salts from alcoholic solutions of the glycoside. R_F (circular) values are 0·77 (phenol saturated with water, 34°), 0·64 (water saturated with phenol, 34°), 0·58 (butanol-acetic acid-water, 40 : 10 : 50, upper layer, 36°) and 0·59 (butanol-acetic acid-water, lower layer, 36°) (Found in a sample dried at 120°: C, 52·9; H, 4·3; $C_{22}H_{22}O_{13}$ requires C, 53·4; H, 4·5%).

Hydrolysis.—The glycoside (0·15 g.) was boiled under reflux with aqueous sulphuric acid (50 c.c.; 7%) for 2 hours. The aglucone was taken up in ether and the aqueous solution exhaustively extracted with ether. On removing the solvent, the extract gave a yellow solid residue (0·1 g.) which crystallised from aqueous alcohol as yellow needles, m.p. and mixed m.p. with patuletin, 260–61°. R_F and mixed R_F 0·77 (phenol saturated with water, 34°) and 0·45 (water saturated with phenol, 34°). Acetate, m.p. and mixed m.p. with patuletin acetate, 176–78°. The aglucone was methylated using dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium. The methyl ether crystallised from aqueous alcohol as colourless needles, m.p. and mixed m.p. with O-pentamethyl patuletin, 141–42°.

The aqueous acid solution was divided into two equal portions. One portion was neutralised with barium carbonate, filtered and the filtrate was concentrated to small bulk (25 c.c.). R_F and mixed R_F with glucose 0·56 (phenol-water, 9 : 1, 30°). With phenyl hydrazine acetate, the solution yielded glucosazone, m.p. and mixed m.p., 205° (d.). The second portion

was neutralised with sodium bicarbonate and titrated against standard Benedict' reagent; the yield of glucose agreed with the requirements of a monoglucoside.

Methylation of the glucoside and hydrolysis.—A finely powdered suspension of the glucoside (0·1 g.) in anhydrous acetone (50 c.c.) was boiled with dimethyl sulphate (1 c.c.; excess) and anhydrous potassium carbonate (3 g.) for 50 hours till the product gave no ferric chloride colour. The semi-solid residue, obtained by filtration and distilling off the solvent from the filtrate, was boiled with aqueous sulphuric acid (50 c.c.; 7%) for 2 hours. There was clear solution and a colourless solid separated out gradually from it. It was taken up in ether, the solution shaken up with aqueous sodium carbonate (5%) and the carbonate extract acidified. When the product was extracted with ether and the solution evaporated a colourless solid (50 mg.) was obtained. It crystallised from alcohol as colourless long plates and needles, m.p. 231–33° (Found in a sample dried at 110°: C, 62·1; H, 5·3; $C_{20}H_{20}O_8$ requires C, 61·9; H, 5·2%). It did not give any ferric reaction. Rao and Seshadri[5] reported 234–35° as the melting point of 7-hydroxy-3:5:6:3′:4′-pentamethoxy flavone obtained by a similar treatment of quercetagitrin.

Ethylation.—The partial methyl ether (25 mg.) was boiled with diethyl sulphate (0·2 c.c.) in anhydrous acetone (25 c.c.) in the presence of anhydrous potassium carbonate (1 g.) for 4 hours. The ethyl ether crystallised from acetone-benzene as colourless rectangular plates, m.p. 128–30°, and mixed melting point with a synthetic sample[4] of 7-ethoxy-3:5:6:3′:4′-pentamethoxy flavone was undepressed.

SUMMARY

A new glucoside has been isolated from the flowers of *Tagetes patula*. It yields by direct hydrolysis patuletin and glucose and by hydrolysis after complete methylation 3:5:6:3′:4′-O-pentamethyl quercetagetin, characterised also as its ethyl ether. The glycoside is, thus, patuletin 7-monoglucoside and is, therefore, named patulitrin.

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PEROXY TITANIUM OXALATE

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Mazzucchelli and Pontanelli[1] prepared a peroxy titanium oxalate complex of the formula $Ti_2O_3(C_2O_4)_2$ from a reddish oil, obtained by adding an excess of hydrogen peroxide, ethyl alcohol and ether to a solution of freshly precipitated titanic oxide in oxalic acid. Literature does not indicate any subsequent work on the peroxy titanium oxalate complexes. The complex, $Ti_2O_3(C_2O_4)_2$, could be considered as a derivative of the peroxy product, Ti_2O_5 which has been shown recently to be the decomposition product of the peroxide TiO_3 on storage.[2] In the present investigation, the method of preparation of the normal peroxy titanium oxalate and its properties are described.

When a solution of precipitated titanium hydroxide in excess of oxalic acid was treated with hydrogen peroxide, it was noticed that an orange red solution was obtained. The depth of the colour depended on the concentration of the hydrogen peroxide added. The absorption spectrum of the solution was different from that of the peroxy titanium sulphate solution investigated by Weissler.[3] The solid could not be crystallized out from the solution but an amorphous red solid was, however, obtained by evaporation of the solution on a water-bath at 50° C. The solid, thus prepared, was found to have variable composition with respect to peroxy oxygen, even though excess of hydrogen peroxide was employed during the preparation. Exact conditions had, therefore, to be worked out for the preparation of a pure peroxy complex.

Experimental

Reagents Employed

1. *Oxalic Acid* (*C.P.*) was recrystallised thrice from distilled water and employed in the preparation of the complex.

2. *Hydrogen Peroxide.*—30% H_2O_2 (Merck) was used.

3. *Pertitanic Acid.*—The yellow pertitanic acid was precipitated by addition of dilute ammonia to an aqueous solution of purified titanium tetrachloride containing the calculated amount of hydrogen peroxide. The pertitanic acid, thus prepared, could be freed from chloride ions by repeated

washing with distilled water but ammonium ions could not be completely removed in this way. The precipitate was, therefore, initially washed with 0·001 N hydrochloric acid which facilitated the removal of ammonium ions. Final washing was effected with distilled water to remove the last traces of the chloride ions. Pertitanic acid free from chloride and ammonium ions was employed for the preparation of the peroxy compounds of titanium. The purified pertitanic acid, prepared from several samples of titanium tetrachloride, had the approximate composition Ti_2O_5 (Table I).

Methods of Analysis

Estimation of Peroxy Oxygen.—Since the peroxy titanium oxalate complex was found to be slightly hygroscopic, precautions were taken to exclude moisture during weighing and transferring the complex. Peroxy oxygen in the complex was determined by the acidified potassium iodide method.[4]

Abel[5] has pointed out that oxalic acid is oxidised to CO_2 by iodine. But experiments carried out in this laboratory on the mixtures of iodine and oxalic acid, both in the dark and in diffused daylight, indicated that there was no detectable oxidation of the oxalic acid by the aqueous iodine. Hence, it was inferred that oxalic acid did not interfere with the estimation of peroxy oxygen by the iodide method.

Estimation of Oxalate.—When the peroxy titanium complex was treated with dilute sulphuric acid, a mixture of hydrogen peroxide and oxalic acid was produced. The sum of the two was estimated by potassium permanganate titration. It is interesting to note in this connection that the estimation of oxalic acid could be carried out rapidly at the laboratory temperature (23° C.) without heating the mixture. This is perhaps due to the catalytic effect of manganese sulphate which is produced during the hydrogen peroxide reduction by permanganate. Since the peroxy oxygen was estimated by the iodide method, the oxalate content could be computed.

Estimation of Titanium.—The peroxy titanium oxalate was ignited in a platinum crucible and the titanium dioxide produced was determined to compute the value of titanium.

Analysis by the Combustion Method.—Since the peroxy titanium oxalate complex contained inactive oxygen, the amount of water in the complex could not be obtained by difference. To determine water in the complex, combustion method was employed using about 50 mg. samples, when water and carbon dioxide produced during the combustion were absorbed by magnesium perchlorate and ascarite respectively. From the values of carbon

dioxide and water, the oxalate and water contents were computed. The titanium content of the complex was estimated by weighing the titanium dioxide residue in the boat. Since the peroxy oxygen, titanium, oxalate ($C_2O_4^{=}$) and water in the complex were known, the inactive oxygen was calculated by difference. The results of analyses by the wet methods and the combustion method agreed well.

Preparation of the Peroxy Titanium Oxalate Complex.—About 30 g. of the slurry of pertitanic acid (Ti = 2 g.) whose molar ratio of TiO_2: O (peroxy) was approximately 1·7 : 1, was mixed with large excess of oxalic acid (14 g.), when an orange red solution was obtained on shaking for about an hour. On concentrating the solution by passing dry air, most of the excess of oxalic acid was crystallised out. Concentration of the solution on water-bath had to be avoided to prevent the oxidation of oxalic acid by the peroxy oxygen. The mother liquor on further concentration yielded an orange red solid (peroxy titanium oxalate), containing some free oxalic acid, which was removed by repeated washing with alcohol. The sample was dried and analysed. The experiment was repeated with different samples of pertitanic acid and the results are given in Table I, where experiments 1 to 3 show that the

TABLE I

Expt. No.	Molar composition of the pertitanic acid used ($\approx Ti_2O_5$)		Molar composition of the red solution after addition of $H_2O_2 + H_2C_2O_4$			Average molar ratio of the various constituents in the solid complex				
	TiO_2	O*	Ti_2O_5	H_2O_2	$H_2C_2O_4$	Ti	O*	C_2O_4	O	H_2O
1	1·67	1	1·0	..	3·70	1·99	1·0	1·94	2·07	6·85
2	1·70	1	1·0	..	2·33	2·14	1·0	2·06	2·07	7·40
3	1·63	1	1·0	..	2·50	2·09	1·0	2·03	1·88	6·90
4	1·70	1	1·0	1·00	2·00	1·52	1·0	1·51	1·35	5·50
5	1·63	1	1·0	1·00	2·05	1·43	1·0	1·45	1·24	4·90
6	1·65	1	1·0	1·50	2·25	1·38	1·0	1·47	1·21	4·20
7	1·75	1	1·0	1·86	2·26	1·12	1·0	1·13	0·99	3·81
8	1·63	1	1·0	1·90	2·92	1·00	1·0	1·10	0·98	3·40
9	1·65	1	1·0	1·98	3·00	1·09	1·0	1·09	0·97	3·42
10	1·70	1	1·00	2·02	3·10	1·08	1·0	1·00	0·93	3·40

* O = Peroxy oxygen obtained by KI Method.

complex has the average composition $Ti_2O_3(C_2O_4)_2$, 7 H_2O. The lower peroxy content of the complex is obviously due to the lower peroxy oxygen content in the titanium peroxide employed as the starting material.

Preparation of Pure Peroxy Titanium Oxalate Complex.—In this series of experiments, attempts were made to increase the amount of peroxy oxygen by addition of hydrogen peroxide in the starting solution, the rest of the procedure being the same as described above. The results are given in Table I, experiments 4 to 10.

The results of the last three experiments (8 to 10) show that in presence of large excess of hydrogen peroxide, the composition of the complex is $TiO_2C_2O_4$, 3·5 H_2O. On the other hand, when the amount of hydrogen peroxide added is low (experiments 4 to 7), the peroxy oxygen content in the final product obtained is less than the theoretical value of the complex $TiO_2C_2O_4$.

Tests for Ascertaining the Peroxide Linkage in the Complex.—Active oxygen in the peroxy complex may be present as perhydrate, where active oxygen is due to the hydrogen peroxide of crystallisation. Active oxygen may also be present as a peroxide forming a true peroxide linkage –O–O–. In order to find out the nature of the peroxy oxygen in the titanium oxalate complex, the following tests were carried out.

(1) *Ether Extract.*—Ether extract[6] of the aqueous solution of the normal peroxy complex did not give any test for hydrogen peroxide, showing that the complex is not a perhydrate.

(2) *Vapours of the Complex Collected in Vacuum.*—The peroxy complex was subjected to evacuation at room temperature for three hours and the vapours evolved from the complex condensed in a trap surrounded by liquid air. The aqueous condensate was free from any hydrogen peroxide, as tested by the titanium sulphate solution.

(3) *Krauss and Oettner Test*[7] *modified by Liebhafsky*[8].—Liebhafsky has stated that when potassium iodide reaction is carried out at a pH of 7·5–8·0, quantitative liberation of iodine would result only in the case of true peroxy compound, while oxygen is liberated when the compound contains hydrogen peroxide of crystallisation. When this test was applied to the peroxy titanium oxalate complex, it was noticed that iodine was liberated and not oxygen. It can, therefore, be concluded that the present complex is a true peroxy complex. Similar tests were given by the complexes containing lower peroxy oxygen content.

Effect of Storage on the Peroxy Complex.—It was observed that the complex faded in colour on storage, obviously due to the loss of peroxy oxygen. To study the rate of decomposition, the peroxy complex, 1·16 Ti: 1·00 (peroxy): 1·15 C_2O_4: 3·80 H_2O, was kept in a weighing bottle in a desiccator free from moisture and the titanium and active oxygen contents were determined daily for about twelve days. The results of Fig. 1

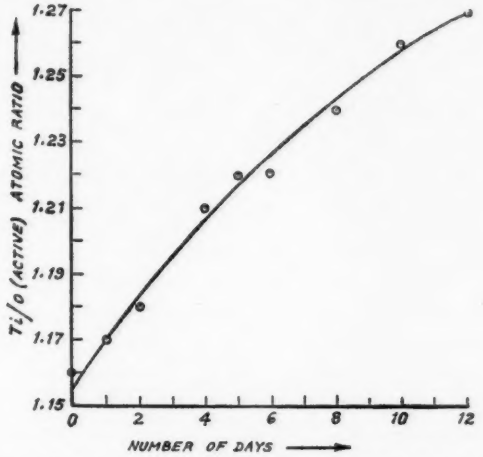


FIG. 1. Variation in Ti:O (Active) Atomic Ratio of the Complex with Time.

show that there is a continuous loss of active oxygen from the complex. The analysis of the substance after twelve days showed that there was practically no loss of oxalate and water and the composition corresponded to 1·3 Ti: 1·00 (peroxy): 1·3 C_2O_4: 4·4 H_2O. Further on long storage, the substance first turned yellow and finally yellowish white. The analysis of the yellowish white product showed that it was basic oxalate, having the formula $TiOC_2O_4$, 3·4 H_2O. It is thus obvious that the peroxy complex, on losing the active oxygen changes itself into basic oxalate. These studies further show that it is difficult to prepare a very pure peroxy complex whose molar ratio of Ti: O (peroxy): C_2O_4: O (non-peroxy) is 1:1:1:1, since it gradually loses the peroxy oxygen. Hence for carrying out physico-chemical studies the peroxy complexes had slightly lower values of active oxygen.

Determination of the Molecular Weight of the Peroxy Titanium Oxalate Complexes.—The molecular weights of the three peroxy titanium oxalates having varying amounts of active oxygen were determined cryoscopically in aqueous solutions using Beckman's apparatus. The results are given in Table II.

TABLE II

Molecular Weights of the Peroxy Complexes by Cryoscopic Method

(*a*) *Complexes Employed*

Complex	Molar ratio					Approximate formula of the complex
	Ti	O (Peroxy)	C_2O_4	O	H_2O	
A	1·13	1·0	1·13	1·18	3·80	$TiO_2C_2O_4$, 3·5 H_2O
B	1·53	1·0	1·50	1·68	5·48	$Ti_{1·5}O_{2·5}(C_2O_4)_{1·5}$, 5·5 H_2O
C	2·09	1·0	2·10	2·02	6·64	$Ti_2O_3(C_2O_4)_2$, 6·5 H_2O

(*b*) *Freezing Point Data of the above Complexes*

Complex	Weight of the complex/100 g. of H_2O (g.)	Lowering of F. pt. (ΔT)	Mole. weight found	Av. mole. weight found	Calculated mole. weight from the formula
A	0·3464	0·027	234·5		
	0·9647	0·077	231·5	230·0	231·0
	1·1140	0·092	224·0		
B	0·4320	0·028	287·0		
	0·8898	0·055	301·0	293·3	243·0
	1·0200	0·065	291·9		
C	0·4136	0·025	307·7		
	1·0250	0·063	302·6	304·1	437·0
	1·3000	0·080	302·2		

The results of Table II show that with complex A, the average molecular weight (230) found is practically equal to the calculated value, assuming the formula of the normal peroxy complex as $TiO_2C_2O_4$, 3·5 H_2O. In the

case of substances B and C, the observed molecular weights are lower than the calculated values.

Spectral Characteristics of the Peroxy Titanium Oxalate Complexes.— The absorption spectra for the three peroxy titanium oxalate complexes (Fig. 2, complexes A, B and C) having different active oxygen content, were

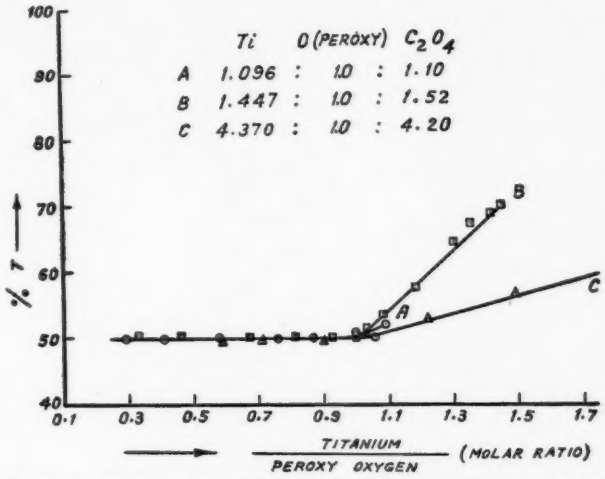


FIG. 2. Effect of Hydrogen Peroxide on per cent. Transmittance of the Complexes.

determined by Coleman model 14, Universal Spectrophotometer. It was found that the absorption maximum for the three complexes was at the wavelength 425 mμ. Employing a reference solution containing hydrogen peroxide and oxalic acid, transmittance (T) measurements were made for various dilutions of the three complexes at 425 mμ. It was found in all the cases that when the solution was dilute (up to 25–30 p.p.m. of Ti), Beer's law was obeyed. Further, when log T (for the three complexes at various dilutions) was plotted against peroxy oxygen present in the complexes, it was found that practically all the three curves coincided. This indicated that in the three complexes the log T was a function of the peroxy oxygen (taking same amount of Ti for the three complexes) present in the complex.

The effect of added hydrogen peroxide on the transmittance of the three complexes was then studied. The results given in Fig. 2 show that the transmittance of the three complexes remains constant when the atomic ratio of Ti: O (peroxy) reaches 1 and less. This study indicates that the normal complex $TiO_2C_2O_4$ is formed only when the ratio of Ti: O (peroxy) is 1: 1 in all the three complexes. It may be noted here that the excess of

oxalic acid or hydrogen peroxide over the stoichiometric amounts present in the normal peroxy complex ($TiO_2C_2O_4$) neither altered the absorption maximum nor did they materially affect the transmittance of the normal complex for a given concentration of titanium.

Conductivity Studies on the Peroxy Titanium Oxalate Complexes.—The molecular conductivity of the three complexes (composition given in Fig. 3) was determined at various dilutions in aqueous solution at 25° C. The results are represented in Fig. 3. The molecular conductivity at infinite

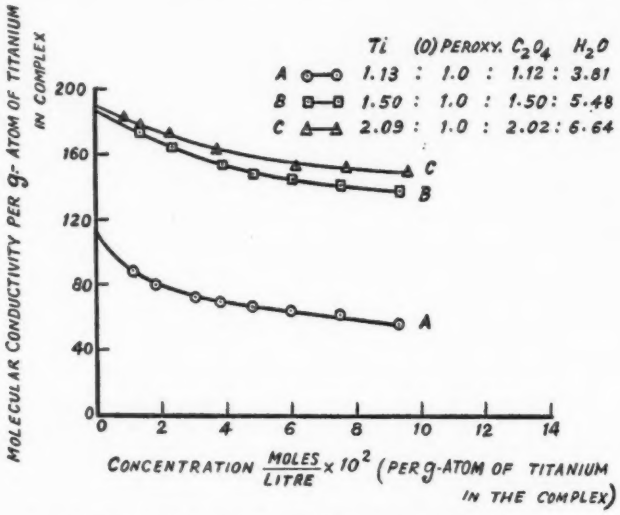

Ti (O) PEROXY. C_2O_4 H_2O
A 1.13 : 1.0 : 1.12 : 3.81
B 1.50 : 1.0 : 1.50 : 5.48
C 2.09 : 1.0 : 2.02 : 6.64
MOLECULAR CONDUCTIVITY PER g-ATOM OF TITANIUM IN COMPLEX
200
160
120
80
40
0
0 2 4 6 8 10 12 14
CONCENTRATION MOLES/LITRE x 10^2 (PER g-ATOM OF TITANIUM IN THE COMPLEX)

FIG. 3. Conductivity of Peroxy Titanium Oxalate Complexes.

dilution is found by extrapolation of the curve A and the degree of dissociation for the normal complex is calculated. The extrapolated value for the conductivity of a normal complex at infinite dilution is found to be 110. The average dissociation constant K for the normal complex was calculated to be $4{\cdot}5\times10^{-2}$ while that for oxalic acid is $K_1 = 5{\cdot}9\times10^{-2}$, indicating thereby that the complex has practically the same order of the degree of dissociation as that of oxalic acid. The molecular conductivity for a given titanium content is much higher in the case of the peroxy complexes B and C than for the normal peroxy complex alone. As stated later, this is due to the association between the peroxy complex and the basic oxalate producing a new complex which may have higher value for the degree of dissociation.

Potentiometric Titration of the Peroxy Complex.—For the potentiometric titration, 25 ml. of aqueous solution containing 322 mg. of the peroxy com-

plex 1·13 Ti: 1·00 (peroxy): 1·20 C_2O_4: 2·97 H_2O were taken. The titration was carried out using the glass electrode to determine the pH of the solution, after each addition of the standard (0·1041 N) sodium hydroxide solution. Δ pH/Δ *vs.* V is plotted in Fig. 4 which shows two points of

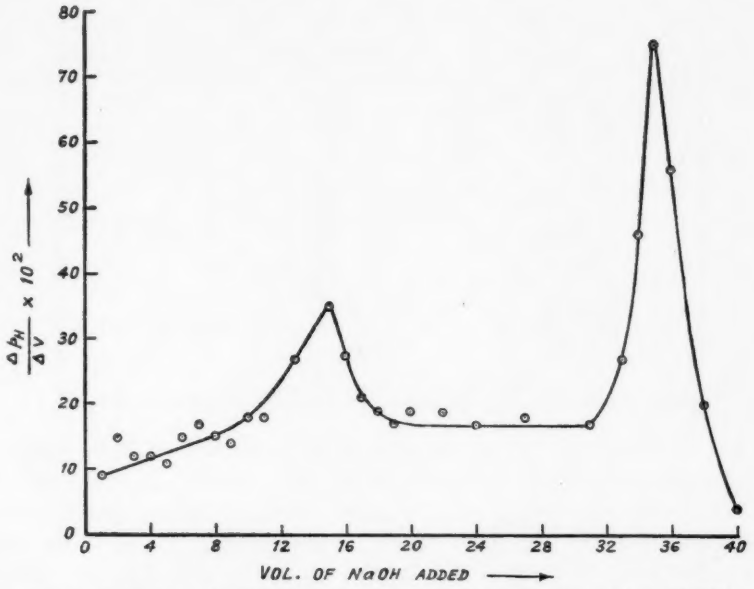


FIG. 4. Potentiometric Titration of Peroxy Titanium Oxalate against NaOH.

inflections, indicating the dibasic character of the complex. During the titration, the solution was clear till the first peak was passed and afterwards the solution became turbid due to the formation of yellowish white pertitanic acid. The turbidity went on increasing till the second peak was reached.

Vapour Pressure Measurements of the Peroxy Complexes.—Vapour pressure measurements have been employed extensively to know the nature of the water associated with the chemical compounds. During the preliminary investigation, it was found that the vapour pressure of the complex was practically a linear function of the temperature. Moreover, it was found that the complex gradually gave out small quantities of oxygen. Hence the individual pressures of these two components were determined by a slight modification of the manometric technique.

Apparatus and Procedure.—The all-glass apparatus consisted of a narrow cylinder A (2·5 cm. dia. × 30 cm. ht.) connected to a trap E and a mercury

manometer M as shown in Fig. 5. A Mcbain-Bakr quartz spring S, with a quartz bucket Q at the lower end, was suspended from a glass sphere H supported in the cylinder. The substance (Ca 200 mg.) was placed in the

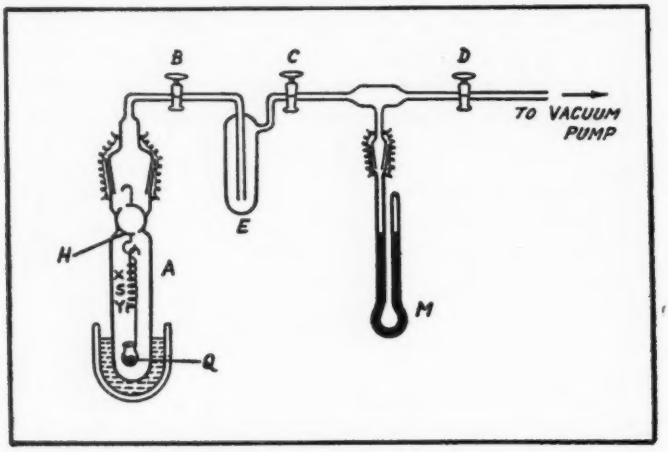


FIG. 5. Apparatus for the Determination of Oxygen Pressure and Vapour Pressure of Peroxy Complex Hydrates.

bucket Q, attached to the quartz spring S and introduced in the vessel A. The whole assembly was fitted up as shown in Fig. 5. The stopcock B was closed and the vessel A was slowly cooled in the liquid air. The stopcock was then opened and the air from the whole assembly was pumped out. The stopcock B was closed again, the refrigeration bath removed and the vessel A allowed to attain the room temperature. The vessel A was again cooled for the second time and it was noticed invariably that during the second cooling with liquid air, the powder would fly out from the bucket due to the rapid freezing of the moisture inside the tube. This difficulty, however, was avoided by admitting small quantities of dry air before cooling. After cooling the vessel A in liquid air, the system was completely evacuated for a period of half an hour to remove the residual air completely. The stopcock D was closed, the cooling bath removed and a water-bath at 2° C. introduced to surround A and the total equilibrium pressure noted at this temperature. In general one hour was sufficient for the attainment of the equilibrium vapour pressure. The stopcock B was then closed and the trap E was cooled in liquid air to condense the moisture in the system between stopcocks B and D. The oxygen pressure was then noted (Fig. 6). The difference between the total pressure and the oxygen pressure gave the aqueous

tension of the complex. In this way, the aqueous tension was determined at temperatures up to 45° C. and the results are given in Fig. 7 where $1/T \times 10^4$

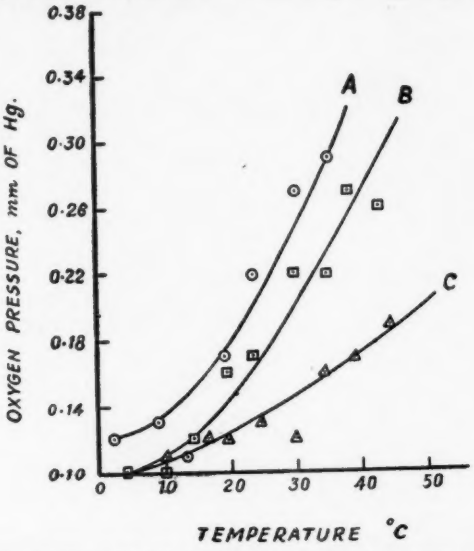


FIG. 6. Oxygen Pressure of the Peroxy Complexes at Various Temperatures.

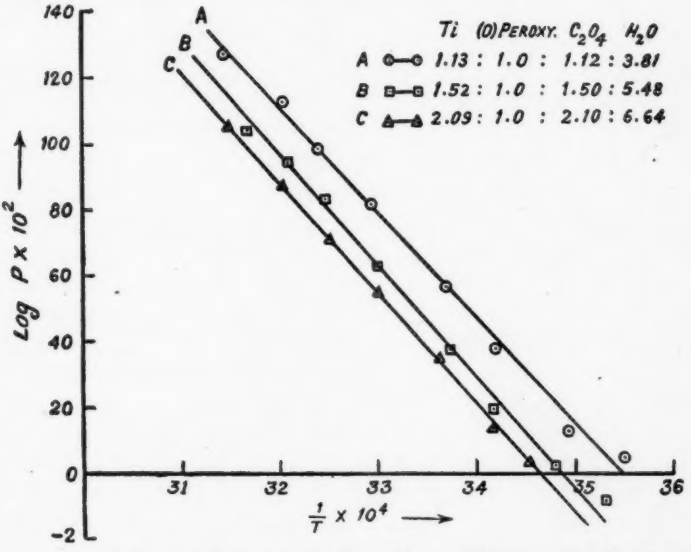


FIG. 7. Effect of Temperature on the Vapour Pressure of Peroxy Complex Hydrates.

is plotted against log $P \times 10^2$. The results of analyses of the substance A, before and after the determination of the vapour pressure, showed that there was little change in the peroxy oxygen content (6·29% to 5·87% peroxy oxygen). From the vapour pressure measurements at different temperatures, the average heat of dissociation for the normal peroxy complex was found to be 15·40 K.cal./mole of water. This was calculated from the slope of the curve A. Similarly the oxygen and vapour pressures were determined for complexes B and C and the corresponding results are given in Figs. 6 and 7 respectively. The heats of dissociation for the complexes B and C were found to be 14·8 and 15·21 K.cal./mole of water respectively.

For complex A, which has got the highest peroxy oxygen content, the oxygen pressure varies from 0·12 to 0·30 mm. of mercury even when the temperature is varied from 2° to 45° C. Thus the oxygen pressure is very low as compared to the aqueous tension of the hydrate for the same range of temperature. Hence in the subsequent study, the oxygen pressure of the complex was not noted while studying the rate of loss of water on continuous evacuation at 25° C.

Rate of Loss of Water from the Normal Peroxy Complex at 25° C.— 200 mg. of the sample [1·06 Ti: 1·00 (peroxy): 1·08 C_2O_4: 3·65 H_2O] was subjected to continuous evacuation and its vapour pressure noted for different water contents of the sample. The loss in weight due to evaporation of water was found out by determining the stretch of the spring (Fig. 5). The sensitivity of the spring was 63·53 mg. for a stretch of 1 cm. Since the loss of peroxy oxygen is very little as compared to that of water from the complex, the loss in weight of the complex due to the loss of peroxy oxygen is neglected. The results are given in Table III.

It is seen from Table III that the fall in vapour pressure is quite rapid till the complex has 3 moles of water, after which the fall in vapour pressure is very slow. Further, the pressure remains practically constant when the complex has about 2 moles of water per atom of titanium. The rate of loss of water at this stage is extremely slow even when evacuation is carried out for comparatively long intervals. When the dehydration of the normal peroxy complex 1·06 Ti: 1·0 (peroxy) : 1·08 C_2O_4: 3·65 H_2O was carried out by keeping the substance over phosphorus pentoxide in vacuum desiccator, it was also noticed that the rate of loss of water was practically negligible, when the complex had 1·8 molecules of water per atom of titanium in the complex. It can, therefore, be concluded that the initial rapid fall in vapour pressure is due to water held in loose combination with the solid. The constancy of the composition and the vapour pressure towards the end of

the experiment indicates that the two moles of water are firmly held by the complex.

TABLE III

Vapour Pressure of the Peroxy Complex

Interval of evacuation in minutes	Moles of water retained by the complex	Vapour pressure mm. of Hg
0·5	3·51	2·81
1·0	3·35	1·72
1·5	3·22	1·34
2	3·18	0·89
3	3·13	0·72
8	3·08	0·38
23	2·93	0·12
38	2·84	0·12
98	2·44	0·15
188	2·34	0·17
278	2·21	0·13
398	2·18	0·12
518	2·15	0·12

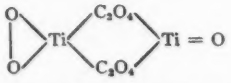
Thermal Studies on the Peroxy Complexes.—The thermogravimetric behaviour of the peroxy titanium oxalate complexes was studied in the modified thermogravimetric balance[9] and it was found that all the three complexes, having varying active oxygen contents, showed three breaks, one at 80–100° C., the second at 250° C., and the third at 320° C., when percentage loss of the substance on heating was plotted against temperature. After 320° C., the curves remained practically horizontal and the residual product on analysis was found to be titanium dioxide.

The products of decomposition formed at the transition temperatures, indicated by the thermogravimetric studies, were determined by collecting

the reactants by means of a Töpler pump. 206 mg. of the normal peroxy complex was taken in a small bulb fused with the Töpler pump. The bulb was cooled by surrounding it in liquid air and the air removed from the apparatus. The substance was then heated to 100° C., and allowed to remain at that temperature for about an hour. At this temperature, no gaseous products of decomposition were obtained. Evidently, this transition temperature indicates the absorption of heat due to loss of water from the complex. Amount of water produced could not be estimated since it was being absorbed by the phosphorus pentoxide kept in the Töpler pump. The temperature was then raised to 250° C., and the substance was allowed to remain at this temperature for about an hour, after which the rate of decomposition slowed down considerably. The gaseous products obtained were collected and analysed for oxygen, carbon monoxide and carbon dioxide. It was found that the gaseous products contained 55·4% CO_2, 38·3% CO and 6·3% O_2. The substance was finally heated to 320° C., when it completely decomposed yielding titanium dioxide and a little carbon in the residue. The gaseous products collected contained 51% CO_2 and 49% CO but no oxygen, showing that all the oxygen was liberated at 250° C.

DISCUSSION

1. *Molar Composition of the Normal Peroxy Complex.*—Mazzucchelli and Pontanelli[1] obtained the compound $Ti_2O_3(C_2O_4)_2$ which was represented as:



In the present investigation, a similar product, having the mole ratio of Ti: O (peroxy): O: C_2O_4 as 2: 1: 2: 2 (Table I, experiments 1 to 3), is obtained, besides two more substances having the mole ratio as 1: 1: 1: 1 and 3: 2: 3: 3 respectively. The results presented in Table I show that the composition of the final product depends on the initial concentrations of the reacting constituents. When a large excess of hydrogen peroxide (Ti: peroxy O as 1: 3 and above) is present in the starting solution, the complex obtained has approximately the composition corresponding to the formula $TiO_2C_2O_4$.

The keeping quality of the normal peroxy complex (Fig. 1) shows that it undergoes decomposition losing peroxy oxygen gradually, while the other constituents remain unaffected. Thus, the peroxy titanium oxalate behaves like pertitanic acid on storage,[2] the difference being that the rate of loss of peroxy oxygen from the peroxy complex is comparatively slower than that from the pertitanic acid. It is, therefore, possible that the substance

reported by Mazzucchelli and Pontanelli is a decomposition product of the normal peroxy complex $TiO_2C_2O_4$ according to the equation:

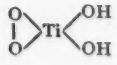
$$4\ TiO_2C_2O_4 \longrightarrow 2\ Ti_2O_3\,(C_2O_4)_2 + O_2 \qquad (1)$$

It is also possible that these authors did not employ a large excess of hydrogen peroxide in the starting solution, which resulted in obtaining a product deficient in peroxy oxygen. The substance $Ti_2O_3\,(C_2O_4)_2$ may be either a mixture of the normal peroxy titanium oxalate, $TiO_2C_2O_4$, and the basic oxalate, $TiOC_2O_4$, in equal proportions or an association complex as shown later. On long storage, the orange red peroxy titanium oxalate is transformed into the white basic oxalate.

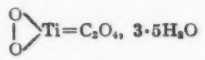
As revealed by the spectrophotometric investigations, the three substances differing in peroxy oxygen content give the same transmittance minimum at 425 mμ. Moreover, the curves represented in Fig. 2 show that the minimum percentage transmittance is obtained when the atomic ratio of Ti: O (peroxy) reached 1 : 1, by addition of hydrogen peroxide to any of the three substances studied. Further addition of hydrogen peroxide does not alter the transmittance of the solution. The identical behaviour of the three substances, therefore, indicates that the normal peroxy titanium oxalate complex has the ratio of Ti: O (peroxy) as 1 : 1. These studies also suggest that any peroxy product which does not conform to the formula $TiO_2C_2O_4$ could be considered as a mixture of the normal peroxy titanium oxalate and its deoxygenated compound. It is seen from Table I that the ratio of water : titanium is maintained at about 3·5, irrespective of the amount of peroxy oxygen in the molecule. The molar composition of the normal peroxy complex can, therefore, be represented as $TiO_2C_2O_4$, $3{\cdot}5\ H_2O$.

2. *Structure of the Normal Peroxy Complex.*—To assign the structure to the peroxy complex, the positions of the peroxy oxygen, the water molecules and the oxalate group with respect to the titanium atom are required to be fixed from the experimental evidences. Further, the structure assigned should conform to the theoretical expectations.

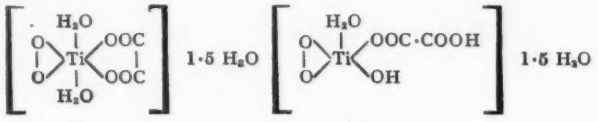
A. *Position of the Peroxy Oxygen.*—Various tests employed to determine the nature of the peroxy oxygen show that the complex is not a perhydrate, but a true peroxy complex, having the peroxy linkage –O–O–. The pertitanic acid from which the peroxy titanium oxalate is derived is represented as,



with two replaceable hydroxy groups. The peroxy linkage in the complex may, therefore, be represented as:



B. *Position of the Molecules of Water in the Peroxy Complex.*—It has been shown that the normal peroxy complex has got 3·5 moles of water, out of which 1·5 moles can be removed by dehydration in vacuum over phosphorus pentoxide. The heat of dissociation (15·4 K.cal./mole of water) for 1·5 moles of water, that are removed on evacuation, shows that the water associated with the complex molecule is combined water. The other two molecules which are difficult to remove in vacuum may be either due to (*a*) the co-ordinated water, or (*b*) partly as co-ordinated and partly as water of constitution. Accordingly, the following two are the possible structures of the peroxy complex:



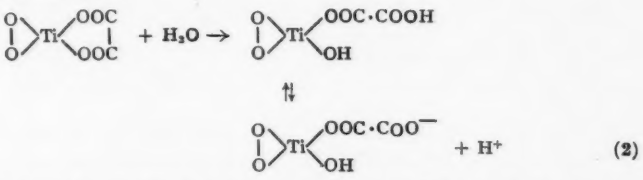
(1) (2)

According to the structure (2) the co-ordination number of titanium is five. In order to obtain a spatially symmetrical arrangement, generally, the co-ordination values of six and four are most usual with various metallic ions. It is, therefore, quite possible that a spatially symmetrical complex with co-ordination number of six as in structure (1) is produced and not as an unsymmetrical complex with co-ordination number five as in structure (2).

C. *Electronic Conception and the Peroxy Complex.*—According to the structure (1), titanium gains eight electrons in the formation of the co-ordination complex. Hence with the twenty-two electrons possessed by the titanium atom, the total number of electrons amount to thirty for the central atom of titanium in the complex. Titanium is expected to attain the electronic configuration of the next higher inert gas, krypton, which has 36 electrons. Cases, however, have been reported in literature where elements forming co-ordination complexes may or may not have the inert gas configuration as in the case of platinous complexes. The main significant factor in assigning the structure is that it should be symmetrical irrespective of the actual number of electrons involved. The structure (1) fulfils this requirement. The normal valency of four for titanium is also satisfied by this structure.

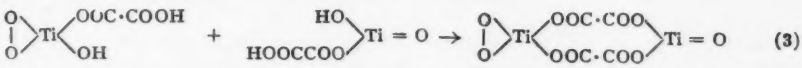
D. *Diamagnetic Character of the Complex.*—Since the electronic structure of the titanium atom in the complex falls short of the electronic configuration of the Krypton gas, one would normally expect the complex to be paramagnetic according to the rule of Welo and Baudisch.[11] Determination of the magnetic susceptibility of the complex by Guoy balance[12] showed that the normal peroxy complex is diamagnetic. It is likely that the electronic configuration of the central paramagnetic titanium ion has undergone redistribution under the influence of penetration due to the approach of the other atoms and molecules. Such redistribution would bring about diamagnetism in the complex.[13]

Nature of the Complex in Aqueous Solution.—The closeness in the values for the dissociation constants of the normal peroxy complex ($K = 4{\cdot}5 \times 10^{-2}$) and oxalic acid ($K_1 = 5{\cdot}9 \times 10^{-2}$) suggests that the peroxy complex ionizes in a similar way as the oxalic acid in aqueous solution. This is due to the hydrolysis of the complex in aqueous solution followed by ionization according to the following scheme:



Another supporting evidence for the above scheme of reactions lies in the fact that the pH of 1% aqueous solution of the peroxy complex is 2·0, showing the acid nature of the complex.

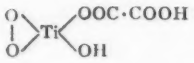
The cryoscopic determination of the molecular weight of the complexes (Table II) show that the substance A, having the mole ratio of Ti: O (peroxy): O: C_2O_4 as 1·1: 1: 1·1: 1 is nearly a pure substance while the substances B and C are contaminated with large amounts of basic oxalate. The higher molecular weights of B and C than that of the normal peroxy complex A are likely to be due to the partial association of the basic oxalate with the peroxy oxalate, according to the equation:



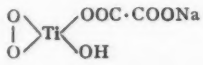
The molecular weight of the normal peroxy complex A is very nearly equal to the theoretical value (Table II), indicating very little dissociation of the complex. This is contrary to the observation made by the conductivity studies where the degree of dissociation is 50%. The low dissociation of the substance A during the freezing point studies can be ascribed to:

(1) the low temperature employed whereby suppression of the dissociation of the complex can result, and (2) comparatively higher concentrations of the substance employed (20 times) in the freezing point experiments, which may result in the association of the complex.

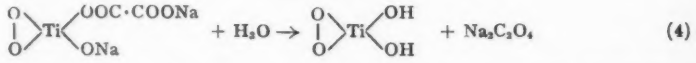
The two peaks observed in the Δ pH/ Δ V *vs.* V titration curve (Fig. 4) can be explained on the basis of the product,



obtained in water medium as per equation (2). When one equivalent of sodium hydroxide (15 ml.) is added to the solution containing the peroxy complex, a soluble mono-sodium complex



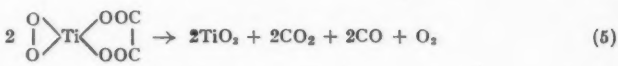
is produced. With further addition of sodium hydroxide, the disodium complex hydrolyses, giving rise to $Na_2C_2O_4$ and TiO_3 as:



(4)

The precipitation of the pertitanic acid continues till the pH of 9·45 is reached, when no more of the peroxy titanium complex will be present in the solution. Thus, the two peaks in the titration curve can be explained on the formation of the mono-sodium salt of the peroxy complex and the pertitanic acid respectively.

Thermal Decomposition of the Peroxy Complex in Vacuum.—The decomposition products obtained while heating the substance in Töpler pump under reduced pressure substantiates the proposed structure. The reaction (5) takes place on heating (in vacuum) followed by two side reductions (6) and (7):



(5)

(6)

(7)

SUMMARY

1. The method of the preparation of the normal peroxy titanium oxalate $TiO_2C_2O_4$, $3 \cdot 5\ H_2O$ is described. If an excess of hydrogen peroxide

is not maintained in the starting solution, substances with the molar compositions $Ti_2O_3(C_2O_4)_2$, $7\,H_2O$ and $Ti_{1\cdot5}O_{2\cdot5}(C_2O_4)_{1\cdot5}$, $5\cdot5\,H_2O$ are obtained.

2. It has been shown by the various physico-chemical studies that the substance $TiO_2C_2O_4$, $3\cdot5\,H_2O$ is a true peroxy complex, while the other two substances are mixtures of the peroxy complex and its deoxygenated product (basic oxalate $TiOC_2O_4$) in different proportions.

3. The keeping quality of the peroxy complex indicates that the complex loses the peroxy oxygen gradually, transforming itself into the basic oxalate.

4. Molecular weights of the three complexes described in (1) have been determined cryoscopically.

5. Conductivity of the aqueous solution of the normal peroxy complex gave the average dissociation constant $K = 4\cdot5\times10^{-2}$.

6. Spectrophotometric investigations on the peroxy complex showed that the peroxy complex has the atomic ratio of Ti : O (peroxy) as 1 : 1 and the absorption maximum of the complex is at the wavelength 425 mμ.

7. Potentiometric titration of the aqueous solution of the complex against sodium hydroxide indicated the dibasic character of the complex in the solution.

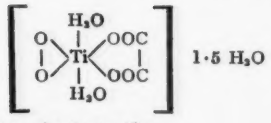
8. Vapour pressure data for the normal peroxy complex gave the heat of dissociation equal to 15·4 K.cal./mole of water, indicating that the water associated with the complex is combined one.

9. Oxygen pressure for the normal peroxy complex varied from 0·12 to 0·30 mm. of mercury in the temperature range 2° to 45° C.

10. Dehydration studies on the normal peroxy titanium oxalate complex in vacuum showed that out of 3·5 moles of water, 1·5 moles are removed from the complex while 2 moles are retained with the complex.

11. Decomposition products obtained on heating the peroxy complex in vacuum are carbon dioxide, carbon monoxide, oxygen, water, titanium dioxide and carbon.

12. The complex has been assigned the structure



based on various physico-chemical studies.

ACKNOWLEDGEMENT

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A STUDY OF THE SOLAR DAILY VARIATION OF MESON INTENSITY AT AHMEDABAD ($\lambda = 13°$ N) USING A CUBICAL MESON TELESCOPE

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Introduction

The Cosmic Ray Sub-Commission of the International Union of Pure and Applied Physics has decided on the establishment of similar standard instruments at a number of stations all over the world for studying the time variations of meson intensity in the lower atmosphere during the International Geophysical Year, 1957–58.

The present paper contains a brief summary of the design and performance of a standard cubical meson telescope which has been installed at Ahmedabad. An attempt has been made to study the daily variation of meson intensity and examine its implications on the anisotropy of the primary radiation.

I. The Experimental Arrangement

The schematic diagram in Fig. 1 shows the arrangement of Geiger counters with their associated electronic units.

The apparatus consists essentially of three trays of Geiger counters forming a triple coincidence arrangement. Each tray consists of twenty counters of diameter 1·6″ and length 36″. The total sensitive area of each tray is nearly 1,300 sq. in. The three trays are arranged one above the other and the distance between the bottom and top trays is 36″. The counters are placed with their axis parallel to the N-S direction; the telescope having semi-angles of 45° in the E-W as well as in the N-S planes. The average counting rate of the telescope is nearly 50,000 three-fold coincidences per hour. Iron plates equivalent to 10 cm. of lead are interposed between the second and the third trays. These cut off the soft component allowing essentially only the μ-mesons to be recorded.

The counter trays are enclosed in a box of thermally insulating compressed fibre sheet. This reduces the fluctuations of the temperature inside the box which is maintained by a thermostat at $108° \pm 2°$ F.

SCHEMATIC OF THE EXPERIMENTAL SET-UP.

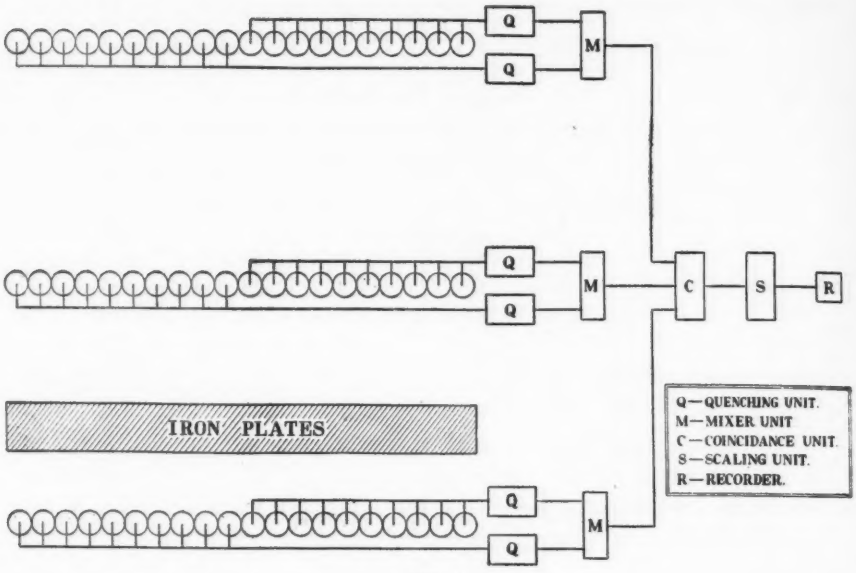

FIG. 1

The twenty counters in a tray are divided into ten sets of two counters each. The anodes of each pair of these counters are connected in parallel to a common one-shot multivibrator. When a cosmic ray particle passes through any pair of counters, the multivibrator delivers a sharp square negative pulse of 300 V and 1,000 μ sec. duration to the central wire of the counters. The output from five such multivibrators is fed through a differentiating network and a cathode follower. Thus the final output is picked up across a resistance in a cathode circuit of this tube. As there are two sets of quenching units Q for each tray, the pulses from both of them are mixed together by a mixing unit M, before being fed to a coincidence unit C. Finally, the triple coincidence output is scaled down by a factor of 128 by a scaler S, before registering it on a mechanical recorder R. The recorder and a clock are mounted on a panel which can be photographed every hour automatically by a 35 mm. camera.

The power supplies which give different voltages to the different electronic units are all regulated against line as well as load fluctuations, to ensure stable operation.

II (*a*). Presentation of Results and Their Analysis

The data sheet for a single day consists of twelve bihourly values of cosmic ray counts and the corresponding record of the ground level barometric pressure.

The useful data presented here cover a period of seven months and are broadly classified into six groups. As the instrument started working towards the end of May 1955, the data for a few days in this month are grouped along with those in June. The different groups and the number of days in each group are indicated in Table I.

Table I

Group	Period	Number of days for which data are available
1	May-June	23
2	July	26
3	August	22
4	September	15
5	October	24
6	November	25

Generally, in the values for a single day, the random statistical fluctuations are greater than the genuine periodic variation. To obtain a significant daily variation curve, values for the same bihourly intervals for all the days in each group are added up and are expressed as percentage deviations from the mean. The final curve thus obtained is fairly smooth and the resulting variation is statistically significant.

In order to examine the phases and the amplitudes of the successive Fourier components of the daily variation, harmonic analysis was made on the twelve bihourly values of each group and each variate separately. These results are summarised in Tables II and III. The bottom row coorresponds to the variation formed by superimposing the data of groups 1 to 6.

II (*b*). Correction for Pressure

Several workers have determined the barometric coefficient from day-to-day variations in cosmic ray intensity. The coefficients for the Carnegie

Institution ionisation chambers vary from $-3{\cdot}0\%$ per cm. Hg for Huancayo to $-1{\cdot}80\%$ per cm. Hg for Cheltenham, Christchurch and Godhavn.

TABLE II

First Harmonic Component of each Variate

Period	Meson Intensity		Pressure	
	r_1	ϕ_1	r_1	ϕ_1
Group 1 ..	0·28%	61°	1·06 mm.	110°
Group 2 ..	0·10%	79°	0·70 mm.	118°
Group 3 ..	0·10%	66°	0·75 mm.	120°
Group 4 ..	0·16%	90°	0·65 mm.	118°
Group 5 ..	0·17%	77°	0·64 mm.	141°
Group 6 ..	0·16%	84°	0·65 mm.	144°
Mean ..	0·15%	80°	0·72 mm.	122°

TABLE III

Second Harmonic Component of each Variate

Period	Meson Intensity		Pressure	
	r_2	ϕ_2	r_2	ϕ_2
Group 1 ..	0·06%	149°	0·73 mm.	−24°
Group 2 ..	0·09%	225°	0·67 mm.	−14°
Group 3 ..	0·10%	188°	0·66 mm.	−23°
Group 4 ..	0·21%	160°	0·84 mm.	−30°
Group 5 ..	0·15%	191°	0·75 mm.	−41°
Group 6 ..	0·14%	138°	0·82 mm.	−35°
Mean ..	0·10%	168°	0·73 mm.	−28°

Sarabhai *et al.*[1] have analysed the meson intensity data of Ahmedabad and Kodaikanal assuming that this value lies between $-1{\cdot}70\%$ per cm. Hg to $-2{\cdot}7\%$ per cm. Hg. After trying various values between these limits, they conclude that a value of $-2{\cdot}2\%$ per cm. Hg may be the most appropriate. Olbert[2] and Trefall[3] have shown that the pressure coefficient can be determined by equating it to the slope of the intensity-depth curve at the appropriate depth of the absorber. These curves indicate that for a thickness of 10 cm. of lead as absorber, β should have a value nearly equal to $-2{\cdot}2\%$ per cm. Hg. This value of β has therefore been taken for correcting the meson intensity data here. Table IV gives the first and second harmonic components of the meson intensity after this correction has been applied.

TABLE IV

Pressure Corrected Values of Meson Intensity M

Period	First harmonic		Second harmonic	
	r_1	ϕ_1	r_2	ϕ_2
Group 1 ..	0·41%	79°	0·10%	−20°
Group 2 ..	0·25%	103°	0·07%	−36°
Group 3 ..	0·23%	105°	0·08%	−72°
Group 4 ..	0·29%	103°	0·05%	−60°
Group 5 ..	0·27%	105°	0·12%	− 5°
Group 6 ..	0·25%	114°	0·05%	−11°
Mean ..	0·29%	102°	0·07%	−56°

III. Discussion of Results

Figure 2 shown below indicates the nature of the daily variation of meson intensity measured with the cubical meson telescope during different groups of days as indicated in Table I.

Figure 2 (*a*) relates to the daily variation before correction and Fig. 2 (*b*) to the variation after applying a correction for the daily variation of barometric pressure using a coefficient of $-2{\cdot}2\%$ per cm. Hg. The last curve in each column represents the daily variation when the data of all groups, 1 to 6 are added together.

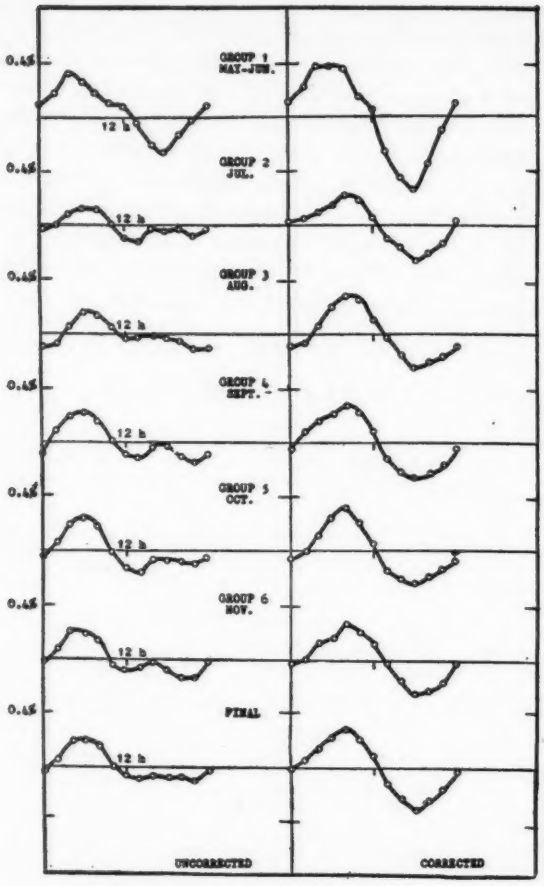

FIG. 2. Daily variation curves for the different groups.
FIGS. 2 (*a*) and 2 (*b*) illustrate the uncorrected and corrected curves respectively.

The harmonic dials in Fig. 3 show the diurnal and semi-diurnal components of the daily variation of meson intensity after applying correction for barometric pressure.

The following facts emerge on examining Figs. 2 and 3 and Tables II and III.

(i) Except for group 1, there is remarkable similarity in the daily variation of meson intensity from group to group. In group 1, the form of daily variation is similar to the other groups but the amplitude s somewhat larger.

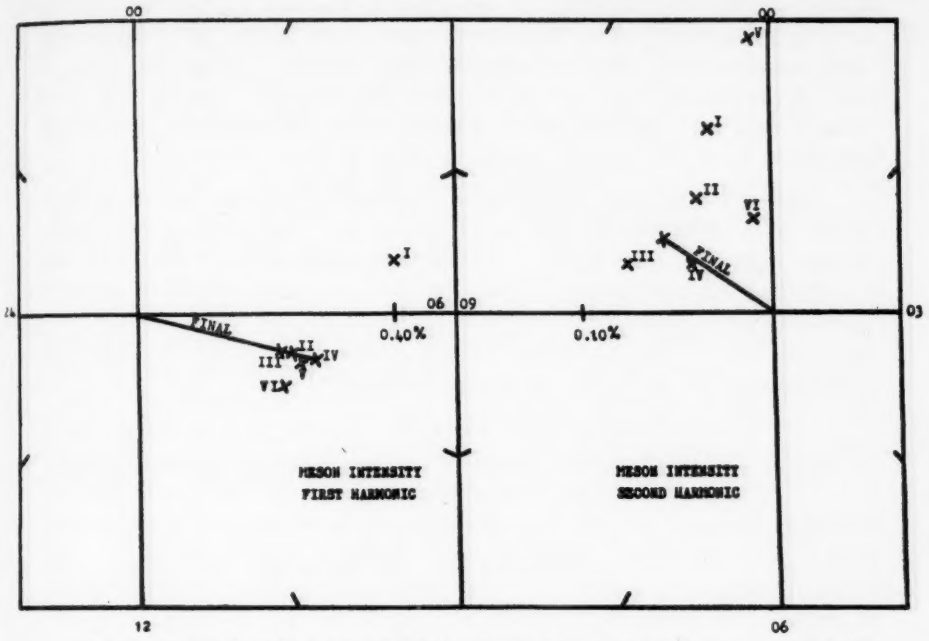

FIG. 3. Harmonic dials showing the first and second harmonics of the meson intensity M, after correcting for pressure.

(ii) Before applying correction for barometric pressure, the daily variation exhibits a principal maximum at about 0400 to 0600 hours I.S.T. There is a small secondary maximum at about 1600 to 1800 hours.

(iii) After correcting for the daily variation of barometric pressure, the daily variation of meson intensity is mainly diurnal in character with only one maximum occurring at about 0800 hours I.S.T.

Thus with pressure correction the small maximum in the afternoon vanishes almost completely, the phase of the early morning maximum is shifted by about two hours towards the later part of the day and the amplitude of the diurnal variation is slightly increased.

Sarabhai *et al.*[1] have reported long-term changes in the nature of daily variation of meson intensity. Hence, comparison with the daily variation with other instruments should only be made during periods when the instruments being compared are simultaneously in operation. During the period June 1955 and July 1955, five other types of instruments were in operation at the Physical Research Laboratory.

In Table V are given the characteristics of the diurnal and semi-diurnal components of the daily variation of meson intensity for all five types of instruments which were simultaneously in operation for two months. All results relate to daily variations after applying correction for barometric pressure.

One of the instruments compared is a meson telescope with a semi-angle of 22° in the E-W plane and 37° in the N-S plane. There were four such telescopes operating. Besides these, the author's colleague Mr. Nerurkar was conducting an experiment to study the daily variation of meson intensity measured with telescopes having semi-angles of 2·5°, 5° and 15° in the E-W plane and 19° in the N-S plane. In addition, Mr. Nerurkar was running a shielded counter tray with omnidirectional sensitivity.

TABLE V

Comparison of the Daily Variation as Measured by Different Instruments during June and July 1955

Instrument	Semi-angle		Harmonic components			
	E-W	N-S	r_1	ϕ_1	r_2	ϕ_2
Omnidirectional ..	90°	90°	0·27%	70°	0·09%	41°
Cube (author) ..	45°	45°	0·29%	102°	0·07%	−56°
Standard unit ..	22°	37°	0·43%	53°	0·19%	92°
Narrow angle—						
(*a*) ..	15°	19°	0·51%	114°	0·17%	49°
(*b*) ..	5°	19°	0·72%	130°	0·25%	75°
(*c*) ..	2·5°	19°	0·78%	134°	0·35%	78°

It will be observed that the per cent amplitude of the diurnal component as well as the semi-diurnal component increases as the semi-angle in the E-W plane becomes progressively narrower. There is not too much difference between the amplitude for an omnidirectional tray and the cubical meson telescope. Also, there is not much difference in amplitude of the telescopes having semi-angles of 2·5° and 5° in the E-W plane. However, the amplitude of the daily variation changes markedly for a change of semi-angle from 5° to 45° in the E-W plane. There might also be some contribution due to the

change of semi-angle in the N-S plane, but at the present moment, excepting in Nerurkar's experiment where the semi-angle in the N-S plane is kept constant, it is difficult to separate the influence of the change of the semi-angle in the E-W and the N-S planes. There is a general tendency for the time of maximum of the diurnal variation to approach noon as the semi-angle of the telescope in the E-W plane becomes narrower. The semi-diurnal variation becomes significant only in the telescopes of moderate to narrow semi-angles in the E-W plane. These results are in conformity with the results obtained by Sarabhai *et al.*[4] and Sekido *et al.*[5]

Day-to-Day Changes in the Daily Variation of Cosmic Rays

It is now well known that the daily variation of meson intensity undergoes several types of changes. Firstly, we have an annual change. Secondly, it has been demonstrated that there are long-term changes which are related to the solar cycle of activity. There are also changes associated with geomagnetic activity. In order to study changes of a day-to-day character, a different method of analysis has been tried.

Following Sittkus,[6] the days were divided into two groups, one having normal and the other abnormal diurnal variation. Days having a daily range of 1% or more in total intensity were classified as abnormal. From a total of 135 days, we had 54 days having abnormal variation. The rest of the days we designate as normal days. The abnormal days were further classified into two sets. These are called the D and N types. D and N stand respectively for days having pronounced day or night maxima. Whenever the diurnal maximum occurred between 0800 and 2000 hours I.S.T., we call it a D-type of day. Similarly, when the diurnal maximum occurred between the hours 2000 and 0800, we designate the particular day as having a night maximum.

The data for each of these sets are harmonically analysed. Table VI gives the values of harmonic coefficients for the different types, according to their classification, after correcting for pressure. Figure 4 illustrates the distribution of vectors on harmonic dials. Figure 5 shows the form of the three types of daily variations, after applying correction for variation of barometric pressure.

The D-type of variation has a maximum at about 1300 hours I.S.T. while the N-type has a maximum at 0400 hours I.S.T. Sarabhai *et al.*[1] have shown that the changes of 12-monthly mean daily variation of meson intensity of Huancayo and Cheltenham are due to the addition or attenuation of a day and a night contribution having maxima at 1300 I.S.T. and 0300 hours

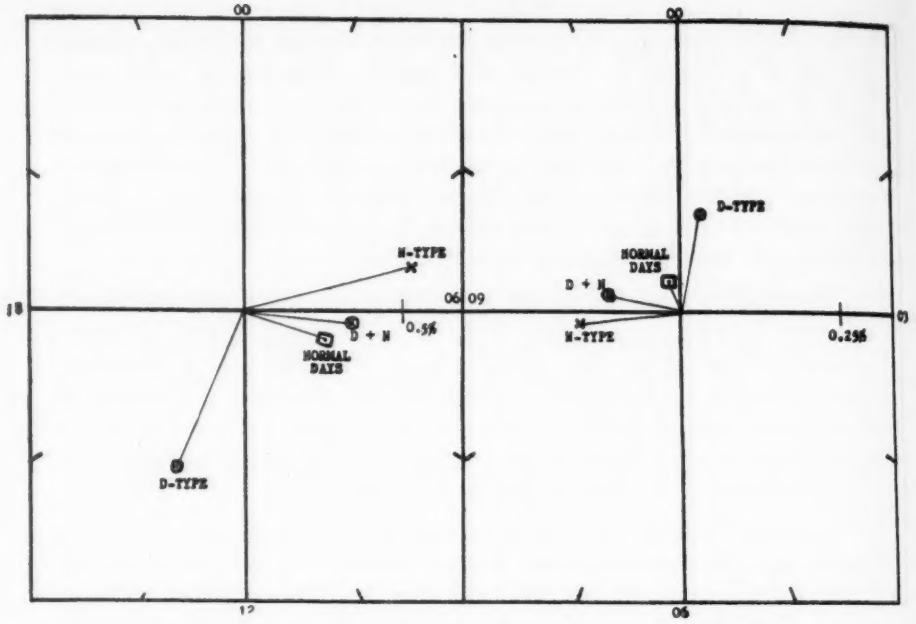

FIG. 4. Harmonic dials showing the first and second harmonics for different groups, after correcting for barometric pressure.

TABLE VI

Pressure Corrected Values of Meson Intensity M, for Different Types

Type	First harmonic		Second harmonic	
	r_1	ϕ_1	r_2	ϕ_2
D ..	$0{\cdot}53 \pm 0{\cdot}04\%$	206°	$0{\cdot}15 \pm 0{\cdot}04\%$	11°
N ..	$0{\cdot}54 \pm 0{\cdot}02\%$	76°	$0{\cdot}16 \pm 0{\cdot}02\%$	263°
(D+N) ..	$0{\cdot}33 \pm 0{\cdot}02\%$	97°	$0{\cdot}12 \pm 0{\cdot}02\%$	−79°
Normal days ..	$0{\cdot}25 \pm 0{\cdot}01\%$	110°	$0{\cdot}05 \pm 0{\cdot}01\%$	−23°

I.S.T. respectively. Thus, our present results which indicate the existence of D and N type of variations is in conformity not only with the studies of Sarabhai, Desai and Venkatesan[1] but also of the investigations with narrow

angle telescopes made by Sarabhai and Nerurkar.[7] Sittkus has not classified abnormal days according to D and N type days. The amplitude and phase as reported by Sittkus corresponds to 0·20% and 1200 hours (8° E meridian time) for the diurnal component.

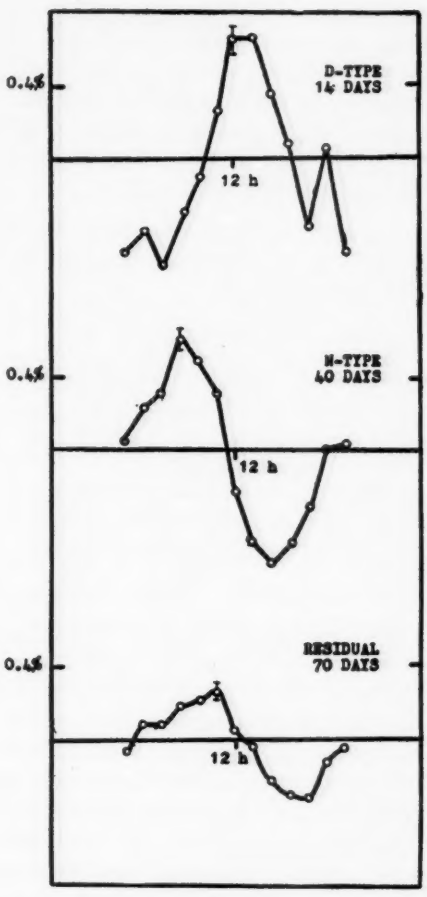

FIG. 5. The three types of daily variation curves, after correcting for pressure.

An analysis made by Sittkus shows that all the days having abnormal values of diurnal variation are not accompanied by high values of K_p. During the period of observation at Ahmedabad, the average magnetic character figure was 0·52 for normal days and 0·55 for abnormal days. Thus, we see

that there is no marked difference in the K_p values for normal and abnormal days, in conformity with the observations of Sittkus.

DIURNAL VARIATION ON MAGNETICALLY DISTURBED DAYS

Sekido and Yoshida[8] have pointed out that days having high magnetic character figure K_p have anomalous diurnal variation. In order to see this, data were further divided into three groups according to the magnetic character figure of the day. Days with K_p values greater than 0·7 formed the first group, those with values between 0·3 and 0·7 the second group and the last group consisted of days having K_p values equal to or less than 0·3. Thus out of a total of 135 days, we had 41 days in the first group, 34 days in the second group and 60 days in the third group.

In Table VII are shown the amplitudes as well as the phases of the diurnal and the semi-diurnal components (corrected for barometric pressure with a value of $\beta = -2{\cdot}2\%$ per cm. Hg).

TABLE VII

Pressure Corrected Values of Meson Intensity M for Different Groups of Days

Type	Mean K_p	First harmonic		Second harmonic	
		r_1	ϕ_1	r_2	ϕ_2
Group 1	1·01	0·31 ± 0·02%	102°	0·07 ± 0·02%	−80°
Group 2	0·50	0·32 ± 0·02%	98°	0·06 ± 0·02%	−42°
Group 3	0·20	0·25 ± 0·01%	106°	0·07 ± 0·01%	−41°

It will be seen that there is no significant difference in the diurnal variation between groups 1 and 2. However, the very quiet days in group 3 are characterised by a smaller diurnal amplitude as observed by Sekido and Yoshida. These authors have reported that for a telescope with semi-angle of 40° in the E-W plane which is similar to ours, the amplitude of the first harmonic increases and the phase advancement amounts to about two hours when K_p changes from 0·00 to 1·80. They have interpreted this result as due to the addition of a new vector, thus introducing a new storm time anisotropy. Yoshida[9] has examined the characteristics of this new vector and found that the amplitude follows the eleven year cycle of solar activity, with negligible amplitude at sunspot minimum. As our experiment was done in

a year immediately after the sunspot minimum, it is possible that the contribution of such an anisotropic vector was small, and hence we do not find much difference in the diurnal variation in groups 1 and 2.

IV. Conclusions

The main points which emerge from the present study may be summarised as follows:

1. During the period June 1955 to November 1955 the mean daily variation of meson intensity, corrected for the daily variation of barometric pressure, as measured by the cubical meson telescope is mainly diurnal in character with an amplitude of ($0{\cdot}3 \pm 0{\cdot}01\%$) and time of maximum at 0800 hours I.S.T.

2. There are significant day-to-day changes in the daily variation of meson intensity. In addition to the normal daily variation of amplitude $0{\cdot}26\%$, there are two distinct types of abnormal variations of large amplitude. These are the D and N types with maxima occurring at 1300 hours I.S.T. and 0400 hours I.S.T. respectively. The amplitude of the diurnal components of these types are $0{\cdot}53\%$ and $0{\cdot}55\%$ respectively. These results are in conformity with those of Sarabhai *et al.*[7]

On the average, days having abnormal daily variations are not associated with a significantly different index K_p of geomagnetic disturbance from the days having normal daily variations. This is in conformity with Sittkus's[6] observations.

3. Except on magnetically quiet days the dialy variation does not show any significant dependence on K_p during the period of observation. The amplitudes as well as the times of maxima of the diurnal components are more or less the same for days having K_p values greater than 0·7 and for days when K_p values lie between 0·3 and 0·7. However, the amplitude of the diurnal component is smaller for days when the K_p value is equal to or less than 0·3. An explanation for this is given on the basis of the interpretation suggested by Yoshida.[9]

Acknowledgement

This work was started and carried out under the direction of Professor Vikram Sarabhai. I take this opportunity to express my sincere and grateful thanks to him for his constant interest, advice and helpful discussions. My thanks are also due to Dr. U. D. Desai, Reader in Electronics at this Laboratory, for helping me in designing the equipment.

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OXIDATIONS WITH SILVER IODIDE DIBENZOATE

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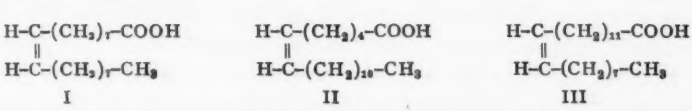
Reaction between silver benzoate and one atomic equivalent of iodine in an inert medium like benzene gives a complex which has been assigned the formula $(C_6H_5—COO)_2AgI$,[1–3] and has been confirmed by Bryce-Smith and Clarke[4] from a study of the hydrolysis of the complex. Prevost[5–7] found that the complex is a powerful oxidising agent and can react with ethylenic compounds to give 1, 2-dibenzoates which give 1, 2-glycols on hydrolysis. The behaviour of the complex towards unsaturated fatty acids and 1, 2-glycols seems to have received no attention so far.

Among the methods available for the hydroxylation of monoethenoid acids the most elegant are those involving the use of dilute alkaline permanganate and the per-acids like performic acid. The action of the former on a *cis*-monoethenoid acid gives the erythro dihydroxy acid by *cis* addition,[8] whereas the oxidation of the same monoethenoid acid with performic acid gives the threo-dihydroxy acid by *trans* addition.[8]

The work under report records the oxidation of three well-known *cis*-monoethenoid fatty acids, Oleic (I), Petroselinic (II) and Erucic (III) with silver iodide dibenzoate.



I II III

It was found that oxidation with the complex in absolutely dry benzene, on the one hand and benzene containing even traces of moisture on the other, gave entirely different results. In carrying out the experiments the 1, 2-dibenzoates were not purified but straight-away hydrolysed to the glycols. The yields of glycols were fairly high in most cases. Oxidation of erucic acid with the complex in absolutely dry benzene gave the lower melting (m.p. 98–99°) threo-dihydroxy behenic acid and no trace of the higher melting (m.p. 129–30°) erythro-dihydroxy behenic acid could be isolated. Oxidation using benzene containing a small quantity of water gave mainly the erythro-dihydroxy acid (m.p. 129–30°) with a lesser proportion of the lower melting

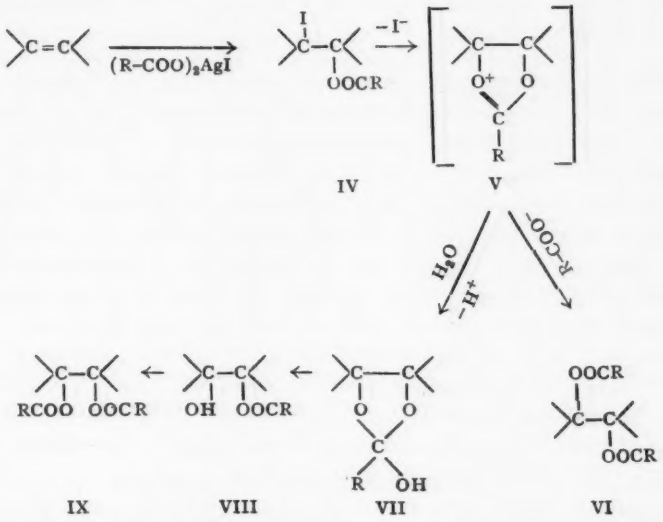
threo-dihydroxy acid (m.p. 98–99°). Repetition of the same experiments with commercial oleic acid and petroselinic acid also gave analogous results, although the yields were poor with the former.

It was established that even traces of mositure in the benzene used for the oxidation would affect the results. This was proved by using benzene dried over calcium chloride in the cold and then distilled. Oxidation of purified oleic acid, petroselinic acid and commercial oleic acid, employing this benzene, gave mixtures containing the corresponding threo- and erythro-acids in each case.

Prevost[5, 6] carried out his reactions on ethylenic compounds in dry benzene and showed that 1, 2-dibenzoates corresponding to *trans* addition are obtained. The present work shows that though Prevost's results are true when absolutely dry benzene is used, in presence of traces of moisture inversion occurs and erythro-dihydroxy compounds (equivalent to *cis* addition) predominate. The stereospecific influence of moisture during the oxidation of an ethylenic bond has been demonstrated in the conversion of *dl*-3-keto-$\Delta^{4,9\,(11),16}$-D-homoandrostatriene to *dl*-3-keto-16 β, 17 β-dihydroxy-$\Delta^{4,9\,(11)}$-D-homoandrostadiene by Barkley *et al.*[9] and in the conversion of (±)-*trans*-menth-2-ene to (±)-*cis*-2-hydroxyneomenthol and (±)-*cis*-2-hydroxymenthol by Jefferies and Milligan,[10] silver acetate-iodine-acetic acid-water being the agent used in these cases.

These inversions in the presence of moisture can probably be accounted for on the basis of the very extensive work of Winstein and Buckles[11] on the role of neighbouring groups in replacement reactions. They have shown that the reaction of silver acetate in dry acetic acid with several acetoxy halides proceeds with retention of configuration, whereas the presence of small amounts of water in the solvent causes inversion to occur. The retention of configuration by using dry acetic acid as the medium and the inversion in the presence of traces of moisture have been accounted for by the participation in the replacement process of the acyloxy group on the carbon atom neighbouring the seat of substitution with the production of an intermediate (V). That (V) may be the intermediate has been supported by the isolation of ortho acetate derivatives[12] in reactions of similar kind. In the presence of dry solvent the reaction of this intermediate with an acyloxy ion gives a product (VI) with the same configuration as the starting material (IV). In presence of traces of moisture, (V) gets converted into (VII), then rearranges to (VIII) followed by O-acylation to (IX). The resultant product assumes a configuration which is the reverse of the starting material (IV). Probably the same mechanism operates in the oxidation of an unsaturated acid with

silver iodo dibenzoate, thus explaining the formation of the threo-compound in the case of oxidation using dry benzene and the production of the erythro-compound as the major product in oxidation using benzene containing traces of moisture.

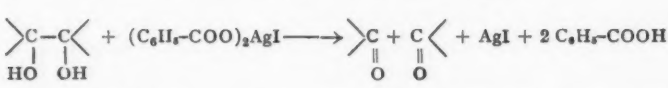


A reversal of configuration has also been observed recently[13] during the conversion of threo-12-bromo-13-acetoxy-oleic acid into erythro-12, 13-dihydroxy oleic acid by the use of silver acetate in wet acetic acid.

That formation of compound (IV) is the first step in the reaction between silver iodide dibenzoate and an ethylenic compound has been shown by Prevost, [7,7a,7b] and this can naturally give rise to an intermediate of the type (V). It was found that even when benzene containing a small quantity of moisture was used, the threo-compound was usually obtained, even though in lesser proportions, on working up the mother liquors after the removal of the major crop of the higher melting erythro compound, which is less soluble. The intermediate for both the threo and erythro compounds may thus be common. Even traces of moisture can affect the results as shown by using benzene which has been dried only over calcium chloride.

The silver iodide dibenzoate used in the present series of oxidations was made *in situ* by warming a solution of iodine in benzene with silver benzoate. The unsaturated acid was then added and the mixture refluxed for a few hours. The resulting products were hydrolysed to the glycols with alcoholic potash, after the removal of the benzene.

A much more important and interesting application of silver iodide dibenzoate was discovered to be its ability to cleave α-glycols giving rise to carbonyl compounds according to the general equation:



To my knowledge this report constitutes the first record of α-glycol cleavage by silver iodide dibenzoate and constitutes one more elegant tool for the step-wise degradation of ethylenic compounds. The reaction is analogous to the cleavage of α-glycols by Criegee's lead tetra-acetate method. Among the compounds that were tried for this type of oxidation were 9, 10-dihydroxy stearic acid; 13, 14-dihydroxy behenic acid; 6, 7-dihydroxy stearic acid, α-monobenzoyl glycerol and hydrobenzoin. In all cases the cleavage was almost complete as judged by the yields of the products obtained. The cleavage proceeded easily in benzene medium and an almost immediate separation of silver iodide occurred when the glycollic compound was added to the bulky, cream-coloured complex in benzene. The reaction was completed by refluxing the mixture for 3–4 hours. The products of the reaction were characterised by the preparation of suitable derivatives. From the reaction mixture benzoic acid was obtained in all cases.

The usefulness of this reagent is quite apparent. Whereas in the case of lead tetra-acetate and periodic acid the glycol has to be prepared by some other oxidising agent, the production of the glycol and its cleavage can both be carried out by using silver iodide dibenzoate, thus making the reagent very useful in the fixation of double bonds.

The application of this new method of oxidation and cleavage is being applied to α-keto-alcohols, α-keto-acids and ethenoid hydro-aromatic compounds like terpenes and sterols.

EXPERIMENTAL

All materials were dried *in vacuo* and benzene over sodium.

Oxidation of Erucic Acid in Dry Benzene

Silver benzoate (4·7 g.) was mixed with powdered iodine (2·5 g.), dry benzene (70 ml.) added and the mixture warmed on the water-bath, taking all precautions against moisture. The colour of iodine disappeared and the cream-coloured silver iodide dibenzoate complex was rapidly formed. To this was added erucic acid (3·4 g.; prepared by the lead salt separation of the mixed acids of mustard oil followed by crystallisation from alcohol) dissolved in a little benzene and the mixture refluxed for 12 hours, moisture

being strictly excluded. After cooling, the benzene solution was filtered free of silver iodide, and the residual silver iodide washed with a little benzene. After removal of the benzene, the residue was refluxed for 45 minutes with 4% alcoholic potash. Most of the alcohol was then removed, the solution diluted with water to 200 ml. and filtered. The clear solution was then acidified with concentrated hydrochloric acid, when the dihydroxybehenic acid was obtained mixed with benzoic and unchanged erucic acids. To remove the benzoic acid the mixture was heated to 80°, the aqueous solution decanted and the residue washed repeatedly with water. The residue was then treated with light petrol to dissolve unreacted erucic acid and filtered to give pale-coloured dihydroxy behenic acid weighing 2·1 g. (56% yield). Crystallisation from ethanol gave threo-13, 14-dihydroxy behenic acid, plates of m.p. 98–99°. There was no depression of the melting point when mixed with the product obtained by performic oxidation of erucic acid. A careful fractional working up of the mother liquor gave only this product and no erythro compound could be isolated.

The method detailed was employed as a general procedure for the oxidation of all the unsaturated acids examined.

Oxidation of Erucic Acid using Benzene Containing a Small Quantity of Water

The complex was prepared from silver benzoate (9·4 g.), iodine (5·0 g.) and 100 ml. of benzene containing 4 drops of water. Erucic acid (6·8 g.) was added and the rest of the procedure was as above. 2·7 g. of crude dihydroxy acid was obtained. Crystallisation from ethanol gave 1·6 g. of a product of m.p. 116–20°, which melted at 129–30° on recrystallisation. This was proved to be erythro-13, 14-dihydroxybehenic acid by mixed melting point with a specimen obtained by dilute alkaline permanganate oxidation of erucic acid according to the method of Doree and Pepper.[14] From the mother liquor a product melting at 92–94° was obtained (0·4 g.) which melted at 98° on recrystallisation from ethanol and proved to be threo-dihydroxybehenic acid.

Oxidation of Petroselinic Acid

Petroselinic acid was obtained from Ajowan seed oil[15] by lead salt separation of the mixed acids. The samples used for oxidation were contaminated with some small quantity of the saturated acids. This contamination is immaterial from the point of view of the present work.

Oxidation using petroselinic acid (2·8 g.), silver benzoate (4·7 g.), iodine (2·5 g.) and 75 ml. of dry benzene gave 1·5 g. of dihydroxy acid (47% yield). Two crystallisations from ethyl acetate gave a product of m.p. 116–17°,

proved to be 6, 7-dihydroxy stearic acid by mixed melting point of this product with that obtained by performic oxidation of petroselinic acid.

Oxidation using 75 ml. of dry benzene containing 3 drops of water gave 1·2 g. of crude dihydroxy acid, which melted at 122–23° on crystallisation first from ethanol and then from ethyl acetate and proved to be erythro-6, 7-dihydroxy stearic acid by mixed melting point with an authentic specimen obtained by oxidation of petroselin-elaidic acid[15] with performic acid. The melting point was depressed to 105–10° on mixing with the corresponding product from petroselinic acid.

Oxidation of Commercial Oleic Acid

Oxidation using absolutely dry benzene gave the threo-9, 10-dihydroxy stearic acid melting at 94°. The use of benzene containing 3 drops of water gave a main crop of erythro-dihydroxy stearic acid of m.p. 130° (from ethanol). The mother liquor afforded the threo-acid of m.p. 90–92°, after repeated crystallisation from ethanol and ethyl acetate. The yields in both oxidations were poor.

Influence of Traces of Moisture on the Course of Oxidation

In a series of experiments in which the benzene used was subjected to only calcium chloride drying, it was found that both the threo and erythro isomers were formed.

Oleic acid was prepared by lead salt separation of the mixed acids from pure olive oil, followed by removal of linoleic acid by barium salt-benzene-95% ethanol method.[20]

Oxidation of oleic acid (2·8 g.) with silver benzoate (4·7 g.), iodine (2·5 g.) and 100 ml. benzene gave 1·4 g. of the dihydroxy derivative. It was separated into two fractions by crystallisation from ethanol, each of which was subjected to repeated recrystallisations from ethanol. The erythro acid of m.p. 132° was obtained from the first fraction and the threo acid of m.p. 95° from the second fraction. Identification of the two was effected by mixed melting points with authentic specimens.

With commercial oleic acid the same results were obtained, but the yields were poor.

Oxidation of petroselinic acid (4·3 g.) gave 2·1 g. of the mixture of dihydroxy acids, which on careful fractional crystallisation from ethanol gave the threo acid melting at 117° and the erythro acid melting at 121-23°. The separation of the two acids required repeated crystallisation.

Oxidation of 1, 2-*glycols*

The following was the general procedure developed:—

Silver iodo dibenzoate was prepared from silver benzoate (4·6 g., 0·02 mole) and iodine (2·5 g., 0·01 mole) by warming on the water-bath with 80 ml. of dry benzene. To the hot mixture was added one molar proportion of the glycollic compound when an almost instantaneous reaction took place in all cases and the bulky cream-coloured complex was replaced by the heavier silver iodide. The mixture was refluxed on the water-bath for 4 hours, all precautions to exclude moisture being taken. The warm benzene solution was filtered free of silver iodide and the products worked up.

Oxidation of 9, 10-*Dihydroxy Stearic Acid* (*m.p.* 132°)

The residual silver iodide after oxidation weighed 4·9 g. (Theory 4·7 g.). Extraction of this with hot ethanol gave only a small quantity of the original dihydroxy acid showing that the reaction is practically complete. After removal of the benzene the residue was steam-distilled, the distillate extracted with ether, the ethereal solution washed with bicarbonate solution followed by water, dried over anhydrous sodium sulphate and the ether removed. The residual unpleasant smelling liquid gave a 2, 4-dinitro-phenyl hydrazone. Crystallisation from ethanol gave golden yellow needles of m.p. 104°. The 2, 4-dinitrophenyl hydrazone of pelargonic aldehyde has been reported to melt at 106–106·5° by King[17] and 106° by Doree and Pepper.[14] Acidification of the bicarbonate washings gave benzoic acid.

The hot aqueous solution from steam distillation was filtered, concentrated to a small bulk and treated with semicarbazide hydrochloride and sodium acetate. The semicarbazone obtained, on crystallisation from alcohol, melted at 162–64° and showed no depression with an authentic specimen of azelaic semialdehyde semicarbazone.

Oxidation of 13, 14-*Dihydroxy Behenic Acid* (*m.p.* 129–30°)

After oxidation the benzene solution was worked up as above. The steam distillate was exhausted with ether, washed with bicarbonate and water, ether removed to yield pelargonic aldehyde identified as its 2, 4-dinitrophenyl hydrazone of m.p. 104–05°.

The residue from steam distillation solidified on cooling. It was repeatedly extracted with boiling water to afford benzoic acid (the more soluble fraction) and brassylic acid (the less soluble fraction). Brassylic acid was identified by its melting point (113–14°)[18] and the melting point of its dianilide (157–58°). The brassylic semialdehyde formed by cleavage has

evidently undergone atmospheric oxidation during working up. This result is somewhat at variance with the observation of Doree and Pepper[14] who found that brassylic semialdehyde formed by oxidation of 13, 14-dihydroxy behenic acid with periodic acid easily underwent polymerisation.

Oxidation of 9, 10, 12-*Trihydroxy Stearic Acid* (*m.p.* 107–09°)

The products of oxidation were worked up exactly as in the first case. The steam volatile product gave a reddish dinitro-phenyl hydrazone of m.p. 123–25°, identified, by mixed melting point, as the dinitrophenyl hydrazone of β-hydroxy-pelargonic aldehyde. The residual solution from steam distillation was filtered and concentrated to a small bulk yielding azelaic semialdehyde semicarbazone, m.p. 164°.

Oxidation of 6, 7-*Dihydroxy Stearic Acid* (*m.p.* 117°)

The benzene solution from the oxidation was washed with three portions of 10 ml. of water, then with 50 ml. of 10% sodium carbonate solution and finally with water. Removal of the benzene gave lauric aldehyde (0·8 g. from 1·5 g. of the dihydroxy acid) identified by preparation of the 2, 4-dinitrophenyl hydrazone (m.p. 103–04°), semicarbazone (m.p. 102°) and oxidation to lauric acid (m.p. 43°). The preliminary aqueous washings of the benzene solution were treated with semicarbazide and concentrated. On keeping rosettes of crystals appeared which, on crystallisation from ethanol, melted at 175–77° (dec.), identified as adipic semialdehyde semicarbazone by mixed melting point.

Oxidation of Hydrobenzoin

1·0 g. of hydrobenzoin yielded 0·7 g. of benzaldehyde, identified as 2, 4-dinitrophenyl hydrazone, m.p. 235°.

Oxidation of α-Benzoyl Glycerol[16]

As the oxidation proceeded there was the smell of formaldehyde which was not identified chemically. The benzene solution, after washing with water and sodium carbonate, yielded a viscous liquid. This gave a semicarbazone in acetic acid medium, m.p. 196–97° (dec.), and produced no depression with the semicarbazone from lead tertra-acetate oxidation (*vide infra*).

Oxidation of α-Benzoyl Glycerol with Lead Tetra-acetate

Benzoyl glycollic aldehyde has been prepared in rather poor yield by the oxidation of α-benzoyl glycerol with manganous sulphate or lead dioxide and hydrochloric acid.[19] It was found that the use of lead tetra-acetate and α-benzoyl glycerol gave better yields in smoother runs. To a solution of

lead tetra-acetate (20 g.) in dry benzene (80 ml.) was added benzoyl glycerol (9·0 g.) with cooling. The mixture was shaken well at intervals and allowed to stand overnight at room temperature. The progress of the reaction was indicated by the smell of formaldehyde and the formation of lead acetate. After 24 hours, the reaction mixture was warmed on the water-bath for 10–15 minutes, cooled and worked up. The residue from benzene gave 6·0 g. of benzoyl glycollic aldehyde as a pleasant smelling colourless liquid on distillation, b.p. 145–47°/16 mm. Semicarbazone, m.p. 197° (dec.).

Summary

Oxidation of erucic, petroselinic and oleic acids with silver iodide dibenzoate in dry benzene resulted in the corresponding lower melting threo-dihydroxy acids, whereas the use of benzene containing a small quantity of water gave mainly the corresponding higher melting erythro-dihydroxy acids. It has been found that even traces of water brought about the inversion for which a probable mechanism is suggested. An entirely new method of 1 : 2-glycol cleavage by the use of silver iodide dibenzoate is described. The method seems to be of general application as indicated by a number of examples worked out.

Acknowledgement

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STUDIES IN THE FORMATION OF HETEROCYCLIC RINGS CONTAINING NITROGEN

Part II. The Position of Methyl Group in the 1: 2-Disubstituted Benziminazole from 4-Methyl-o-phenylenediamine and Benzaldehyde

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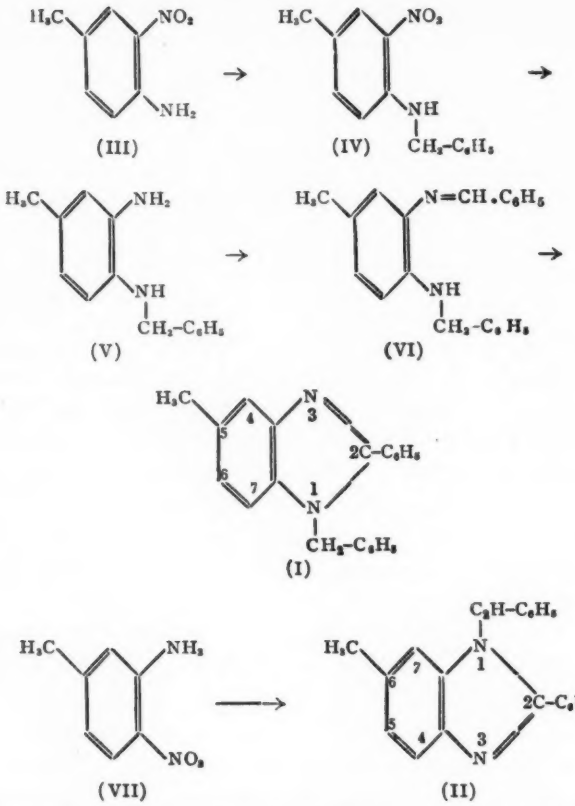
By the condensation of 4-methyl-*o*-phenylenediamine with benzaldehyde, Ladenburg[1] obtained a product, which was proved by Hinsberg[2] to be a 1:2-disubstituted benziminazole. Hinsberg prepared a number of compounds having similar structure by extending the reaction to other aldehydes, but in all these cases, he represented the aromatic part of the ring as $C_7H_6<$, leaving the position of the methyl group uncertain. Later, Pinnow and Wiskott[3] condensed 4-nitro-*o*-phenylenediamine with benzaldehyde and pointed out that two isomeric forms of the disubstituted benziminazole ($-NO_2$ in 5 or 6 position) were possible. They, however, obtained only one product, and did not succeed in their attempts to fix the position of the nitro group in it.

In our systematic investigation of the reaction between 4-methyl-*o*-phenylenediamine and aromatic aldehydes, we were confronted with the assignment of position to the methyl group. As a typical case, the product obtained by condensation with benzaldehyde was studied in detail. When the condensation of the diamine with benzaldehyde was carried out according to the modified Hinsberg's procedure,[4] in addition to the 1:2-disubstituted benziminazole, the 2-monosubstituted benziminazole and a benzodiazacycloheptatriene derivative also could be isolated. The disubstituted compound was found to be identical with that reported by Ladenburg, and it may be either 1-benzyl-2-phenyl-5-methyl benziminazole (I), or 1-benzyl-2-phenyl-6-methyl benziminazole (II). It was felt that the only way of proving its structure would be to prepare the two benziminazoles (I) and (II) by unambiguous methods and compare the condensation product with them.

Synthesis of 1-benzyl-2-phenyl-5-methyl benziminazole has been achieved starting from 3-nitro-*p*-toluidine (III), prepared by well-known procedures.[5] It has been benzylated adopting the procedure used for the benzylation of

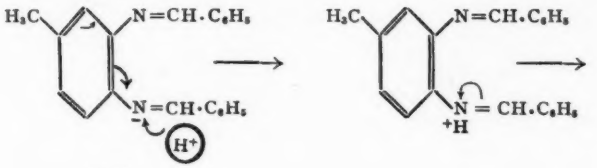


nitranilines,[6] when N-benzyl-3-nitro-*p*-toluidine (IV) is obtained. Reduction of this nitro compound with zinc dust and hydrochloric acid has given rise to 4N-benzyl-3 : 4-tolylenediamine (V), which on condensation with benzaldehyde in alcoholic medium yielded 3N-benzylidene-4N-benzyl-3 : 4-tolylenediamine (VI). By the oxidative cyclisation of this anil (VI) by refluxing in alcohol in the presence of air, or by the direct condensation of the amine (V) with benzaldehyde in alcoholic medium containing nitrobenzene,[7] 1-benzyl-2-phenyl-5-methyl benziminazole (I) has been obtained. Adopting similar procedure, 1-benzyl-2-phenyl-6-methyl benziminazole (II) has been synthesised from 4-nitro-*m*-toluidine[5,8] (VII), through the corresponding benzyl derivative (VIII), diamine (IX) and anil (X).

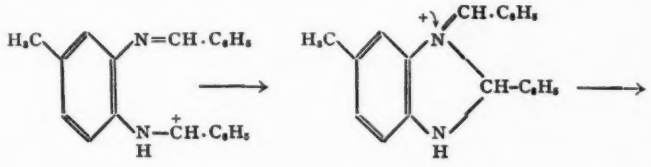
The two benziminazoles thus synthesised differed markedly in crystalline shape and also in melting point. The 1 : 2-disubstituted benziminazole

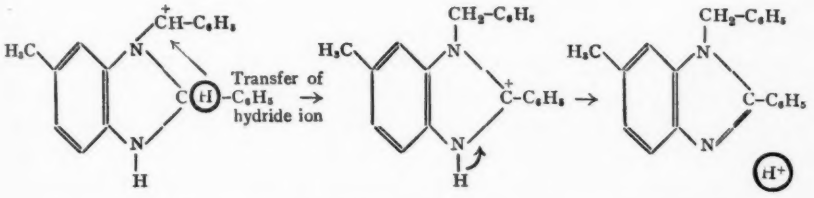
obtained by the condensation of 4-methyl-*o*-phenylenediamine with benzaldehyde was found to be identical with 1-benzyl-2-phenyl-6-methyl benziminazole.

The formation of the 6-methyl isomer instead of the 5-methyl derivative could be explained on the basis of the influence of the methyl group in the aromatic ring of the intermediate dianil (XI). It could reasonably be assumed that the anil para to the methyl becomes active and promotes cyclisation by the transfer of a hydride ion to the carbon atom in the other anil. Such hydride ion migrations seem to be fairly frequent in organic reactions as reviewed recently by Braude.[9] The mechanism of this cyclisation may be represented by the following stages which are initiated by a proton, supplied by the condensing agent, attaching itself to the negatively charged nitrogen para to the methyl group.



(XI)





In general, it may be expected that in all the 1 : 2-disubstituted benziminazoles formed from 4-methyl-*o*-phenylenediamine and aromatic aldehydes, the methyl group will be in position 6.

Experimental

All m.p.'s are uncorrected. The microanalyses were carried out by one of the authors (C. V. R.).

Except the 1 : 2-disubstituted benziminazole now proved to be 1-benzyl-2-phenyl-6-methyl benziminazole and 2-phenyl-5-(or 6-) methyl benziminazole, all other compounds recorded below have not so far been reported in literature.

Condensation of 4-methyl-o-phenylenediamine with benzaldehyde

4-Methyl-*o*-phenylenediamine (1·5 g.) was dissolved in a little more than minimum quantity of glacial acetic acid and benzaldehyde (2·7 g.) added with thorough shaking. The reaction was allowed to proceed at room temperature for one hour with occasional stirring, and by the end of this time a crystalline solid A (0·4 g.) separated out. The mixture was filtered and the clear acetic acid solution poured into a large excess of crushed ice with vigorous stirring and left overnight. A granular solid B (3·0 g.) was obtained and the filtrate on making ammoniacal, gave another product C (0·5 g.).

Solid A, on recrystallisation from a mixture of alcohol and acetone, gave colourless needles, m.p. 160°, and analysed for 2 : 3 : 4-triphenyl-7-(or 8-) methyl benzodiazacycloheptatriene (Found: C, 87·5; H, 6·1; N, 7·6; $C_{28}H_{22}N_2$ requires C, 87·1; H, 5·7; N, 7·3%). Substance B, obtained as colourless prismatic rods, m.p. 195° on recrystallisation from alcohol and benzene, was found to be the 1 : 2-disubstituted benziminazole. The compound C crystallised from alcohol in colourless needles, m.p. 249°, and could be identified as 2-phenyl-5-(or 6-) methyl benziminazole.

1-*Benzyl-2-phenyl-5-methyl benziminazole* (*I*)

(*a*) *N-benzyl-3-nitro-*p*-toluidine* (*IV*).—3-Nitro-*p*-toluidine (III; 15 g.), fused sodium acetate (9 g.), iodine (0·2 g.) and freshly distilled benzyl chloride (13 g.) were thoroughly mixed and heated on a boiling water-bath for twelve hours. The resulting product, while hot, was poured into excess of ice water (200 ml.) and the solid that separated was filtered. The unreacted benzyl chloride was removed by pressing the solid with filter-paper and washing with cold petroleum ether (b.p. 60–80°). The remaining solid was washed with dilute sulphuric acid (1 : 2) to remove the unconverted amine, with water until free from acid, and dried (yield 12 g.). Recrystallisation from petroleum ether gave shining orange-red prismatic rods, m. p. 95° (Found: C, 68·9; H, 5·9; N, 11·3; $C_{14}H_{14}N_2O_2$ requires C, 69·4; H, 5·8; N, 11·6%).

(*b*) 4*N-benzyl*-3 : 4-*tolylenediamine* (*V*).—To N-benzyl-3-nitro-*p*-toluidine (IV; 4 g.) in hot alcohol (50 ml.) was added zinc dust (6 g.). The mixture was kept on a water-bath at 40–50°, and the addition of concentrated hydro-

chloric acid was regulated so that a slow evolution of hydrogen could be maintained (6 hours). The solution was filtered, concentrated to a small volume and poured into excess of water (300 ml.). Concentrated ammonia was added to the clear solution until the precipitated zinc hydroxide redissolved, and the ammoniacal solution was extracted with ether. The ethereal extracts, after drying, were evaporated, yielding crude 4N-benzyl-3:4-tolylenediamine (2·4 g.) as a viscous oil turning brown in air. The hydrochloride was obtained by passing dry hydrogen chloride into its dry ethereal solution and repeatedly washing the product with ether and hot petroleum ether. Recrystallisation from ethylacetate-petroleum ether mixture yielded colourless rectangular rods, m.p. 122° (Found: C, 67·1; H, 7·2; N, 11·0; $C_{14}H_{16}N_2 \cdot HCl$ requires C, 67·6; H, 6·8; N, 11·3%).

(*c*) *3N-benzylidene-4N-benzyl-3:4-tolylenediamine* (*VI*).—4N-Benzyl-3:4-tolylenediamine (V; 0·6 g.) in alcohol (4 ml.) and benzaldehyde (0·3 g.; 1 mole) were heated on a boiling water-bath for fifteen minutes, when a light yellow crystalline solid separated. The mixture was cooled, filtered, and the residue washed with alcohol (yield 0·7 g.); light yellow rectangular rods, m.p. 162° (Found: C, 84·4; H, 6·6; N, 9·0; $C_{21}H_{20}N_2$ requires C, 84·0; H, 6·7; N, 9·3%). Recrystallisation was not carried out since it showed a tendency to undergo oxidative cyclisation resulting in the corresponding benziminazole.

(*d*) *1-Benzyl-2-phenyl-5-methyl benziminazole* (*I*).—

(i) *By the oxidative cyclisation of the anil* (*VI*).—The anil (0·5 g.) was suspended in alcohol (50 ml.) and refluxed for eight hours passing a slow stream of air. The resulting solution was concentrated to one-third of the original volume, cooled and filtered. The residue was found to be mostly the unchanged anil. The filtrate was evaporated and the residue (0·25 g.) thus obtained, on recrystallisation from dilute alcohol and benzene, gave colourless hexagonal prisms of (I), m.p. 157° (Found: C, 84·7; H, 6·4; N, 9·5; $C_{21}H_{18}N_2$ requires C, 84·6; H, 6·1; N, 9·4%).

(ii) *By the condensation of the diamine* (*V*) *with benzaldehyde*.—To the diamine (1 g.) in alcohol (5 ml.) were added benzaldehyde (0·5 g.; 1 mole) and nitrobenzene (10 ml.), and refluxed for one hour. The solution remaining after evaporation of alcohol was steam distilled to remove nitrobenzene, and the residue (1·2 g.) on recrystallisation from alcohol and benzene gave (I) identical in all respects with the product reported in (*d*)-*i*, and different from the condensation product B of 4-methyl-*o*-phenylenediamine with benzaldehyde.

1-*Benzyl-2-phenyl-6-methyl benziminazole* (*II*)

(*a*) *N-benzyl-4-nitro-*m*-toluidine* (*VIII*).—4-Nitro-*m*-toluidine (VII; 15 g.) when benzylated following the procedure used for 3-nitro-*p*-toluidine, gave the crude benzyl derivative (10·5 g.). It crystallised from petroleum ether in orange rhombic plates, m.p. 103° (Found: C, 69·6; H, 5·7; N, 11·4; $C_{14}H_{14}N_2O_2$ requires C, 69·4; H, 5·8; N, 11·6%).

(*b*) 3*N-benzyl-*3 : 4-*tolylenediamine* (*IX*).—Reduction of (VIII), (4 g.) when carried out in a manner similar to that of (IV), resulted in 3N-benzyl-3 : 4-tolylenediamine (2·4 g.), colourless solid, m.p. 52°, rapidly turning dark brown in air. The hydrochloride of (IX) was obtained as transparent rectangular rods from a mixture of acetone and ether, m.p. 192° (decomp.) (Found: C, 67·7; H, 6·9; N, 11·2; $C_{14}H_{16}N_2$.HCl requires C, 67·6; H, 6·8; N, 11·3%).

(*c*) 4N-*benzylidene-*3*N-benzyl-*3 : 4-*tolylenediamine* (*X*).—Condensation of (IX) (0·6 g.) with benzaldehyde (0·3 g.) in alcoholic solution for a period of thirty to forty minutes yielded 4N-benzylidene-3N-benzyl-3 : 4-tolylenediamine (0·7 g.), yellow thick rectangular plates, m.p. 166° (Found: C, 84·4 ; H, 7·1; N, 9·2; $C_{21}H_{20}N_2$ requires C, 84·0; H, 6·7; N, 9·3%).

(*d*) 1-*Benzyl-2-phenyl-6-methyl benziminazole* (*II*)

(i) *By the oxidative cyclisation of the anil* (*X*).—The anil (0·5 g.) on oxidative cyclisation in alcoholic medium gave a compound (0·3 g.) which on recrystallisation from benzene gave colourless glistening prismatic rods, m.p. 197° (Found: C, 84·6; H, 6·4; N, 9·4; $C_{21}H_{18}N_2$ requires C, 84·6; H, 6·1; N, 9·4%).

(ii) *By the condensation of the diamine* (*IX*) *with benzaldehyde.*—The diamine (1 g.) was condensed with benzaldehyde (0·5 g.) in alcohol solution containing nitrobenzene, as in the preparation of benziminazole (I). The crude product (1·3 g.) on purification gave a crystalline compound identical with (II) reported in (*d*)-*i*, and with the condensation product B of 4-methyl-*o*-phenylenediamine with benzaldehyde, mixed m.p. undepressed.

Our thanks are due to Prof. T. R. Seshadri of Delhi University for his helpful suggestions and keen interest throughout this work.

SUMMARY

1-Benzyl-2-phenyl-5-methyl- and 1-benzyl-2-phenyl-6-methylbenziminazoles have been synthesised starting from 3-nitro-*p*-toluidine and 4-nitro-*m*-toluidine respectively. The 1 : 2-disubstituted benziminazole obtained

by the condensation of 4-methyl-*o*-phenylenediamine with benzaldehyde has been shown to be identical with the 6-methyl benziminazole.

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PYROXENES FROM THE CHARNOCKITE KHONDALITE INTERACTION ZONE OF WALTAIR

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Introduction

The charnockites in the present sense of the word include a variety of rock types with diversified mineralogical and textural features but characterised by the presence of the pleochroic orthopyroxene, as an essential mineral constituent. These are represented by the norites and pyroxenites on one end and by the hypersthene granites, granulites, and associated quartz veins on the other. The petrology and petrogenesis of these have been studied in considerable detail and the literature on the topic shows the existence of more than one theory to account for their origin. However, not much attention appears to have been paid to the paragenetical study of the important minerals like the pyroxenes from the different members of the charnockite group in the elucidation of their petrogenesis. Towards the fulfilment of this objective, some of the optical properties of pyroxenes from different types of hybrid rocks as well as some basic charnockites, obtained from an interaction zone between charnockites and khondalites, have been studied. The field relationship of the various types of rocks is also given to serve as background to the paragenetical study.

Location.—Interaction zones of basic charnockites with the khondalite gneisses (quartz-sillimanite-garnet-gneisses) are excellently exposed in some quarries for road metal about a mile N.-W. of the Andhra University, adjacent to the Visakhapatnam-Vizianagaram Grand Trunk Road (N. Lat. 17° 44′ and Long. 83° 19′ in sheet No. 65 0/2, 0/3 and 0/6).

Field relationship.—The quarry affords a unique opportunity to study rocks varying from basic charnockites to the highly felspathic leptynites. The basic rocks being rich in pyroxenes have a deep black or blackish green colour and the leptynites, being rich in quartz and garnet, are greyish white to pinkish white. The variation in colour is not uniform in all parts of the quarry which can be seen in some blotchy leptynites with black patches due

to the localisation of charnockitic material. Lenses varying in size from six inches to four feet consisting of coarse crystals of feldspar and pyroxene occur as local modifications in the charnockites. Similarly large crystals of garnets and feldspars occur in lenticular segregations of similar dimensions in the leptynites. The leptynites grade imperceptibly into khondalite gneisses away from the zone of contact. The charnockites are in the form of bosses, stocks, sills and dykes sending out tongues and apophyses.

The pyroxene-bearing rocks show visible lineation chiefly in their pyroxene content, as is clearly seen in most of the outcrops in the field. The pyroxene-bearing rocks as well as leptynites show local faulting and fracturing. The faults show evidence of relative movements by the presence of smooth linear grooves and slicken sides on the surface of the fault planes.

Petrography of the rock types.—Two distinct rock types, namely the basic charnockites, and khondalite gneisses, and hybrid rocks with varied proportions of alkali and calcic feldspars and pyroxenes, can be seen in the area. On the mineralogical basis these hybrid rocks may be loosely described as 'intermediate' and 'acid' types. The petrographical characters of representative specimens from the above types of rocks, namely Basic, 'Intermediate', and 'Acid' are given in Table I.

TABLE I

Petrography of the Rock Types

S. No.	Type of charnockite	Location at the quarry face	Colour	Specific gravity	Granularity	Texture	Mineralogy
1	Acid medium	Top	Grey	2·67	Medium	Granitic	Perthite, Quartz, Albite, Pyroxene, Garnet and Magnetite
2	Acid coarse	Top to middle (variable)	Grey and black spotted	2·71	Very coarse	Porphyritic	Perthite, Pyroxene, Oligoclase, Quartz, Magnetite and Biotite
3	Intermediate	Middle	Greyish black	2·77	Medium	Hypidiomorphic	Andesine, Pyroxene, Orthoclase, Magnetite, Quartz, Apatite, Biotite and Garnet
4	Basic	Bottom	Greenish black	3·06	Medium	Hypidiomorphic	Pyroxene, Labradorite, Magnetite, Biotite and Amphibole

RESULTS

As the present objective is to describe some of the optical properties of pyroxenes, the above description is intended to give an idea of mineral associa-

tion and environmental factors for each of the types. About 120 grains of pyroxenes from 8 micro-sections representing four types were optically studied by Federov Stage, more particularly with reference to the scheme of pleochroism, optic sign and axial angle, and the angle between the slow vibration direction 'Z' and the '*c*' crystallographic axis. The results are given in Table II.

TABLE II

Summary of the Optical Properties of Pyroxenes

Represents 'n' number of grains	2V	Optic sign	Z ∧ *c*	Extinction angle Z '∧ *c*'	Pleochroism		
					X	Y	Z
Group I—In Acid, Intermediate and Basic Charnockites							
20	60	−ve	0	0	Pink	Green	Green
6	42	−ve	0	0	Brown-pink	Grey	do
1	60	+ve	0	0	Yellow pink	Green	do
3	60	−ve	0	20	Brown	do	do
Group II—In Acid, Intermediate and Basic Charnockites							
1	..	−ve	3	3	Pink	..	Green
3	52	−ve	4	20	Yellow-pink	Grey	do
3	60	−ve	6	8	Pink	do	..
1	80	−ve	7	8	do	Green	Green
6	..	−ve	7	0	do	..	Blue-green
4	44	−ve	8	23	do	Grey	Yellow
1	64	+ve	10	14	do	do	Green
8	60	−ve	12	28	do	do-	Yellow
2	76	−ve	14	29	do	do	Brown
1	..	−ve	16	13	do	..	Yellow
1	40	−ve	18	6	do	Yellow	..
1	66	−ve	20	12	do	Grey	Yellow
Group III—In Intermediate and Basic Charnockites							
5	..	+ve	23	22		Light green	
3	62	+ve	27	43		Greenish yellow	
1	40	−ve	30	20	Yellow	Brown	..
4	60	+ve	32	38		Brownish green	
9	40	+ve	40	22		Green	
6	60	+ve	50	42		do	
1	..	+ve	66	28		do	

It may be stated that during optical work with Federov Stage, the following experimental limitations are met with:—

(1) In the determination of the axial angle, there may be a variation of 4° on account of the presence of slight brush extinction;

(2) The angle Z ∧ *c* has been determined on the assumption that the single cleavage shown by almost all the 120 pyroxene grains that have been

studied, is a vertical cleavage and the '*b*' crystallographic axis coincides with 'Y' ether axis. The former is warranted by the fact that the pole of such a cleavage bears a definite relationship to the poles of the ether axis; and

(3) In most cases the cleavages are not well defined and clear, such that, in bringing them to vertical position as indicated by their sharpness, a variation of about 2° to 3° in the tilt is present.

The results show that many of the pyroxene grains are pleochroic from pink along X through grey-yellow in the Y to green along the Z directions. Some of the grains specially in the basic charnockites show blue-green to pale green colours with no distinct pleochroism. All of the pyroxenes in the acid and intermediate charnockites and some of the grains in the basic charnockite are optically negative with an axial angle of 40°–80°. The other pyroxene grains in the basic charnockite are optically positive with an axial angle of 40°–62°. Many of the optically positive grains are non-pleochroic.

The $Z \wedge c$ angle of many pyroxenes in the acid and intermediate rocks is zero whereas some grains show $Z \wedge c$ angles between 0° and 24°. The $Z \wedge c$ angle in the basic charnockites show a gradual variation from 0° to 66°. Some of the grains with $Z \wedge c$ angle zero show up to 20° 'extinction angles' (measured with respect to the traces of cleavage planes on sectional planes of the grains). A few of the grains with zero 'extinction angle' show up to 9° $Z \wedge c$ angle. In the case of other pyroxene grains, the $Z \wedge c$ angle and 'extinction angle' differ in varying degree.

Discussion

Field Relationship and its Significance.—The mode of occurrence of the charnockites appears to suggest that the basic charnockites were probably in the nature of a primary intrusive and 'intermediate and acid charnockites', so called, are merely the result of the assimilation of varied amounts of the pre-existing rocks, by the basic charnockite and reconstitution, resulting in types that may mineralogically be described as 'intermediate and acid'. The use of these terms should not therefore be taken to imply any normal igneous differentiation as the nomenclature may indicate. There appears to be a strong suggestion in this interesting area of the activity of magmatic juices and emanations in the process of the replacement of the pre-existing rock, and pyrometasomatic activity appears to have been of recognisable magnitude. As may naturally be expected for such a zone of interaction, all variations, from chilled and gradational contacts, through xenoliths, streaky and blotchy, and other types of hybridization to complete assimilation

and reconstitution of the reacting rocks are met with. At the contact of the charnockite and khondalite there appears to be refusion of khondalite with permeation in the margin resulting in the formation of a granulitic rock which may be described as leptynite.

'Z $\wedge$c' *value and* '*extinction angle*'.—The 'extinction angles' show great variation with regard to the corresponding Z $\wedge c$ values in some cases. The only possible explanation for this anomalous result appears to be that the optic plane is not parallel to the sectional plane of the crystal wherever the Z $\wedge c$ value and the 'extinction angle' do not coincide, and where the sectional plane is parallel to the optical plane, the 'extinction angle' will have a value equal to the Z $\wedge c$ value. This is well explained stereographically by Johannsen with regard to the oblique extinction in orthopyroxenes. By the same process of argument and analogy it may be explained that in the case of clinopyroxenes also, the anomalous observation of straight extinction and variation from the Z $\wedge c$ value results from the non-coincidence of the optical plane with the sectional plane.

Is there an intermediate group of pyroxenes between the rhombic types and clinœnstatite hedenbergite groups?

In the pyroxenes studied there is variation in the '2 V' as well as Z $\wedge c$ values. The variation in the '2 V' is between 40° and 80° which is reported by previous workers. On the other hand the angle Z $\wedge c$ shows a progressive variation between 0° and 66°. The pyroxenes of 'intermediate and acid' charnockites have Z $\wedge c$ values, ranging between 0° and 24°, and many of them have a zero value. These pyroxenes are pleochroic and negative. But, the basic charnockites contain pyroxenes optically positive, nonpleochroic or weakly pleochroic, with Z $\wedge c$ values ranging between 24° and 66°, and also a few pyroxenes with Z $\wedge c$ values 0° and between 0° and 24°, common in acid and intermediate types.

For convenience of description, these pyroxenes can be divided into three groups on the basis of Z $\wedge$ *c* value, pleochroism, and optical nature; a first, the orthopyroxenes (hypersthenes) with Z $\wedge$ *c* value 0°, with distinct pleochroism, and negative sign, a second, clinopyroxenes (clinœnstatite, diopside and hedenbergite series) with Z $\wedge$ *c* value more than 21°, nonpleochroic or weakly pleochroic, and optically + ve, and a third group of clinopyroxenes with Z $\wedge$ *c* value between 0° and 21°, pleochroic, and optically negative. A few grains, in their optical nature, are exceptions. The pyroxenes of the third group, with low Z $\wedge c$ values and high 2 V values with recognisable pleochroism and optically negative nature, seem to be complex in nature and do not fit into any of the isomorphous groups of pyroxenes de-

scribed by Winchell. In common with the first and the second groups, they have the same range in optic axial angles. Like the second group and unlike the first group, they belong to the monoclinic system. Like the first group and in contradiction to the second group they are pleochroic, optically negative and have Z $\wedge$ *c* values less than 22°. Thus they appear to be a linking group between the well-known ortho- (first group) and clino- (second group) pyroxenes and are evolved in the process of paragenesis due to interaction of the charnockites and khondalites.

Summary and Conclusions

(1) In the neighbourhood of Waltair, the relationship between charnockites and khondalites is excellently revealed in some road metal quarries. The field study has shown that the charnockites occur in the form of bosses, stocks, sills and dykes, intrusive into khondalites, producing all stages of hybridization and assimilation, resulting in the formation of varied types of hypersthene-bearing rocks.

(2) The optic axial angle, optical sign, pleochroism and Z $\wedge$ *c* value are determined for about 120 grains of pyroxenes in basic 'intermediate', and 'acid' charnockites.

(3) The pyroxenes studied can be classified into three groups based on the above optical data.

(i) Orthopyroxenes with Z $\wedge$ *c* value 0°, with distinct pleochroism and negative sign.

(ii) Clinopyroxenes with Z $\wedge$ *c* value more than 21°, nonpleochroic or weakly pleochroic and optically positive.

(iii) Clinopyroxenes with Z $\wedge$ *c* value between 0° and 21°, pleochroic and optically negative.

Groups one and two correspond to the well-known ortho- and clinopyroxene groups as described by Winchell.

Group three is similar to orthopyroxenes (group one) in pleochroism and optic sign. It is similar to group two in that it belongs to monoclinic system.

It differs from group two in optic sign and pleochroism and from group one in the system of crystallisation.

It is unique in that the Z $\wedge$ *c* angle for this group (group three) is intermediate between the known ortho- and clinopyroxenes. In this respect it is a class by itself not described or reported so far.

It is suggested from the optical characters that this is a link between the orthopyroxenes on the one hand and known types of clinopyroxenes on the other and therefore a new group.

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COMPARISON AND EVALUATION OF THE ABSOLUTE VALUES OF PARAMAGNETIC RESONANCE ABSORPTION IN SOME POWDERS

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1. Introduction

The magnitude of paramagnetic resonance absorption in various substances varies considerably. Most of the measurements reported in the literature, however, are given in arbitrary units as a function of the magnetic field. It would be of interest to compare the amount of absorption among various substances and evaluate the absorption in terms of absolute units in order to understand the nature of paramagnetic resonance absorption in more detail. Previous efforts in measuring the absolute values of paramagnetic absorption include those of Cummerow and others (1947) and Kumagai and others (1954). Their methods consisted in measuring the Q of the cavity resonator and its changes due to the introduction of the sample. The method gives rough values of χ'' (the imaginary part of the complex susceptibility giving rise to absorption). The inaccuracy in the method is mainly due to the uncertainty of the form factor. The method is also tedious and is not widely applicable. As for most purposes, comparison of χ'' of any substance with that of a suitably chosen standard substance (whose value can be determined independently and accurately once and for all) is enough, a simple method of comparing the paramagnetic resonance absorptions has been tried successfully and the results are given in this paper.

2. Experimental Method

The principle of the method is to resolve the absorption curve of a mixture (of known weights of the substance under investigation and a suitably chosen standard substance) into two curves of appropriate heights by knowing the *form* of the individual absorption curves.

The total absorption (say Z_1) of the mixture at a field H_1 can be expressed as

$$m_1X_1 + m_2Y_1 = Z_1 \qquad (1)$$

where X_1 and Y_1 are the absorptions of the individual components and m_1 and m_2 are their respective masses, had they been taken under identical conditions. Similarly we can write

$$m_1X_2 + m_2Y_2 = Z_2 \tag{2}$$

at a different field H_2.

From a pair of independent measurements on pure substances, we can get $X_1/X_2 = \alpha$ and $Y_1/Y_2 = \beta$ and substituting these in the two equations we can solve for the *ratio* X_1/Y_1. It is given by

$$\frac{X_1}{Y_1} = \frac{\alpha}{\beta}\frac{m_2}{m_1}\frac{(\beta Z_2 - Z_1)}{(Z_1 - \alpha Z_2)} \tag{3}$$

It is to be noted that in order that the two equations (1) and (2) may be solved for the ratio they should be linearly independent. This requires that the shapes of the paramagnetic resonance absorption curves of the two substances being compared, be different.

The experimental set-up is the same as described in a previous paper by the author (Sundaramma, 1955) except for the following modifications. All the measurements have been made at 9195 Mc/S.

1. To keep the current steady, the current for the magnet coils has been supplied from a set of heavy duty storage batteries.

2. The current has been measured very accurately by means of a potentiometer reading to 0·1 millivolt in conjunction with a standard resistance 0·1 ohm.

In addition to the above, the magnet has been calibrated by means of proton magnetic resonance and the klystron power supply has been electronically regulated to maintain the microwave power and frequency steady. All these refinements are essential for getting reliable data. It should be noted that even small shifts of the curves with respect to one another will produce composite curves of different shapes and so utmost care has to be exercised not only in obtaining the data but also in having the microwave frequency very constant. Also the choice of the two fields H_1 and H_2 at which the ordinates X, Y, Z's are read off has to be made carefully. Steep portions of the curves, or points far removed from the resonance peak (where the accuracy is not enough) have to be avoided. It is better to choose the mass ratio in the mixture such that both the substances contribute substantially equally to the absorption.

The choice of the standard substance has to be made carefully. In the present investigation manganous sulphate monohydrate has been chosen

TABLE I

Substance X	Substance Y	Mass ratio $\frac{m_y}{m_x}$	Peak to peak ratio gram mole per gram mole [X/Y]	(Average)	Ratio of the peak to peak absorption gram mole/gram mole from area measurements [X/Y]	Ratio of the relaxation times (from Gorter) [X/Y]
1. $MnSO_4 \cdot H_2O$	$CuSO_4 \cdot 5\,H_2O$	0·84	6·2			
,,	,,	4·66	6·9	6·53	7·04	10·5
,,	,,	12·92	6·5			
2. $MnSO_4 \cdot H_2O$	$K_2Cr_2(SO_4)_4$ 24 H_2O	4·35	3·62			
,,		3·34	3·55	3·59	3·59	4·0
,,	,,	9·75	3·01			
,,	,,	30·20	4·19			
3. $MnSO_4 \cdot H_2O$	$Cu(NH_4)_2(C_2O_4)_2$ 2 H_2O	2·54	6·62			
,,	,,	5·44	5·6	6·36	6·20	..
,,	,,	10·55	6·86			
4. $K_2Cr_2(SO_4)_4$ 24 H_2O	$CuSO_4 \cdot 5\,H_2O$	2·66	1·65	1·65 (1·82 cross-check from 1 and 2)	2·08	2·62

because the substance has been thoroughly investigated by many workers. Its g. value is accurately known and it has a broad simple resonance curve which is quite different from many other salts. The water of hydration of the sample of manganese sulphate used was experimentally determined and it is the monohydrate ($MnSO_4 \cdot H_2O$).

3. Results

Measurements have been made on well powdered specimens of copper sulphate ($CuSO_4 \cdot 5\ H_2O$), chrome alum [$K_2Cr_2\ (SO_4)_4 \cdot 24\ H_2O$] and cupric ammonium oxalate [$Cu\ (NH_4)_2\ (C_2O_4)_2 \cdot 2\ H_2O$], with manganous sulphate monohydrate ($MnSO_4 \cdot H_2O$) as the standard. In order to check the method, a mixture of chrome alum and copper sulphate was studied. Table I gives the results obtained for the various substances, as also its comparison with that obtained from zero field magnetic susceptibility data.

4. Discussion

An estimate of the value of paramagnetic resonance absorption can be made by the application of Kramers' theorem, *i.e.*, the relationship

$$\chi'(0) = \frac{2}{\pi} \int_0^\infty \frac{\chi''(H)\, dH}{H}$$

where $\chi'(0)$ is the zero field susceptibility, $\chi''(H)$ is the field dependent part of the complex susceptibility leading to absorption. To a first approximation, the magnetic field H in the denominator of integrand can be taken as a constant and replaced by H_m, the resonance field and the integral replaced by the area under the absorption curve. Such estimates have been made by Cummerow and others, Kumagai and others in the papers already referred to. In order to effect a more accurate comparison of the absolute values of χ'' among various substances, the integral has been graphically evaluated in the present investigation without making the above-mentioned approximation. The results are presented in Table II and compared with the previous data in Table III. For purposes of comparison the approximate calculations are also presented. Ratios of the susceptibilities have also been given and it is found that Kramers theorem is valid to within a few per cent.

Table III summarises the data so far obtained and gives the values of χ'' in absolute units.

Spin-spin interaction is the main cause of line spreading and a correlation between spin-spin relaxation time and the peak value of absorption

can be expected. Spin-spin relaxation times have been taken from Gorter (1947) and been entered in Table I with other results.

TABLE II

Substance		Ratio of the integrated absorption gram mole/gram mole X/Y		Ratio of the susceptibilities gram mole/gram mole X/Y
X	Y	From approximated Kramers theorem	Kramers theorem	
$MnSO_4 \cdot H_2O$	$CuSO_4 \cdot 5\ H_2O$	9·06	9·25	9·72
,,	$K_2Cr_2(SO_4)_4 \cdot 24\ H_2O$	2·42	2·36	2·39
,,	$Cu(NH_4)_2 \cdot (C_2O_4)_2 \cdot 2\ H_2O$	10·91	11·2	10·99
$K_2Cr_2(SO_4)_4 \cdot 24\ H_2O$	$CuSO_4 \cdot 5\ H_2O$	4·38	3·56	4·07

TABLE III

Value of absorption (χ'' per mole) in cm.^{3} $\times$ 10^2 Powder data

Substance	Cummerow and others	Kumagai and others	Author	
			From area measurements	From ratios w.r.t. to $MnSO_4 \cdot H_2O$
$MnSO_4.H_2O$	14·0 (4 H_2O ?)	14·3	15·67	..
$CuSO_4.5\ H_2O$	1·73	..	2·19	2·40
$K_2Cr_2(SO_4)_4.24\ H_2O$	..	..	4·365	4·35
$Cu(NH_4)_2(C_2O_4)_2.2\ H_2O$	..	..	2·51	2·71

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5. SUMMARY

By the simple method of measuring the absorption of mixtures of the powders of copper sulphate pentahydrate, chrome alum and cupric ammonium oxalate dihydrate with manganous sulphate monohydrate, their paramagnetic resonance absorption have been compared with that of manganous sulphate monohydrate. The peak to peak ratios gram mole/gram mole and the ratios of the integrated absorption have been evaluated. By applying the Kramers relation between the zero field susceptibility and the integrated absorption the absolute values of χ'' have been evaluated and their ratios agree well with those determined in the present investigation. These values have been correlated with relaxation time and susceptibility.

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UMBILICAL INDICATRICES OF THE UNIT TANGENT VECTOR AND THE PRINCIPAL NORMAL AND BINORMAL VECTORS OF A CURVE IN RIEMANNIAN SPACE

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Section 1

Let V_n be a hypersurface of a Riemannian space V_{n+1}. Let $(x^1, x^2, \ldots, x^n)$ be the co-ordinates of a point P of V_n, whose Riemannian metric is $ds^2 = g_{ij}dx^i dx^j$. Let $ds^2 = a_{\alpha\beta}dy^\alpha dy^\beta$ be the Riemannian metric of V_{n+1} and $(y^1, y^2, \ldots, y^{n+1})$, the co-ordinates of any point on it.

Since V_n is a hypersurface of V_{n+1}, $y^\alpha = y^\alpha\ (x^1, x^2, \ldots, x^n)$, $(\alpha = 1, 2, \ldots, n+1)$ and $g_{ij} = a_{\alpha\beta}y^\alpha{}_{;i}y^\beta{}_{;j}$, $(i, j = 1, 2, \ldots, n)$.

Let C be a curve of V_n, e^i the components of the unit tangent vector to C in V_n and $E^\alpha = y^\alpha{}_{;i}\, e^i$, the components of the unit tangent vector to C in V_{n+1}.

Consider the locus of points whose co-ordinates are $(E^1, E^2, \ldots, E^{n+1})$. The locus of such points is a curve $\bar{C}$ in the hyperquadric Q_n defined by $a_{\alpha\beta}E^\alpha E^\beta = 1$.

We shall prove that Q_n is a hypersurface of umbilics. Let $\bar{N}^\alpha$ be the normal vector at a point $[E^1, E^2, \ldots, E^{n+1}]$ of Q_n and lying in V_{n+1}.

$$\bar{N}_\alpha = \text{grad}\,(a_{\alpha\beta}E^\alpha E^\beta) = E_\alpha.$$

Therefore the vector $\bar{N}$ is co-directional with the vector E.

$\bar{\Omega}_{ij}$, the fundamental tensor of the hyperquadric Q_n, is given by $\bar{\Omega}_{ij} = a_{\alpha\beta}E^\alpha{}_{\bar{;}ij}\bar{N}^\beta$, where $\bar{;}$ denotes tensor differentiation with reference to Q_n.

$$\therefore\quad \bar{\Omega}_{ij} = a_{\alpha\beta}E^\alpha{}_{\bar{;}ij}E^\beta, \text{ since } \bar{N} = E.$$

Since E is a unit vector of V_{n+1}, we have

$$a_{\alpha\beta}E^\alpha E^\beta = 1.$$

Differentiating covariantly w.r.t. Q_n,

$$a_{\alpha\beta}E^{\alpha}E^{\beta}_{\bar{;}i} = 0.$$

Differentiating again,

$$a_{\alpha\beta}E^{\alpha}_{\bar{;}i}E^{\beta}_{\bar{;}j} = -\,a_{\alpha\beta}E^{\alpha}E^{\beta}_{\bar{;}ij} = -\,\bar{\Omega}_{ij}.$$

But,

$$a_{\alpha\beta}E^{\alpha}_{\bar{;}i}E^{\beta}_{\bar{;}j} = \bar{g}_{ij}$$

where $\bar{g}_{ij}$ is the metric tensor of Q_n.

$\therefore\ \bar{g}_{ij} = -\,\bar{\Omega}_{ij}$ at every point of Q_n.

$\therefore\ \bar{C}$, the image of C, is a curve locus of umbilics.

This being true for all curves C of V_n, it follows that Q_n is hypersurface of umbilics.

Since the unit normal vector at a point of $\bar{C}$ is co-directional with the tangent vector to C at the corresponding point, we call $\bar{C}$ as the *umbilical indicatrix* of C. The process is the generalization of the spherical indicatrix of a skew curve in ordinary space.

THEOREM 1. *The arc elements of $\bar{C}$ and C are connected by the relation $d\bar{s}^2 = 1/\rho^2\, ds^2$, where $1/\rho$ is the first curvature of C in V_{n+1}.*

Proof.—Since $\delta E^{\alpha}/\delta\bar{s}$ are the components of the unit tangent vector to $\bar{C}$ in V_{n+1}, we have,

$$a_{\alpha\beta}\,\frac{\delta E^{\alpha}}{\delta\bar{s}}\,\frac{\delta E^{\beta}}{\delta\bar{s}} = 1.$$

It is easily proved that

$$\frac{\delta E^{\alpha}}{\delta\bar{s}} = \frac{\delta E^{\alpha}}{\delta s}\,\frac{ds}{d\bar{s}}$$

$$\therefore\ a_{\alpha\beta}\,\frac{\delta E^{\alpha}}{\delta s}\,\frac{\delta E^{\beta}}{\delta s}\left(\frac{ds}{d\bar{s}}\right)^2 = 1,$$

i.e.,

$$a_{\alpha\beta}\,\frac{\theta^{\alpha}}{\rho}\,\frac{\theta^{\beta}}{\rho}\left(\frac{ds}{d\bar{s}}\right)^2 = 1, \quad \text{by the Serret-Frenet formula.}^{1}$$

$$\therefore\ d\bar{s}^2 = \frac{1}{\rho^2}\,ds^2.$$

THEOREM 2. *The unit tangent vector to $\bar{C}$ is co-directional with the unit principal normal vector to C in V_{n+1}, and the ratio of torsion to curvature at any point of C is equal to the geodesic curvature of $\bar{C}$ at the corresponding point.*

Proof.—

$\bar{E}^a$, the unit tangent vector to $\bar{C}$

$$= \frac{\delta E^a}{\delta \bar{s}} = \frac{\delta E^a}{\delta s}\frac{ds}{d\bar{s}} = \frac{\theta^a}{\rho}\cdot\rho \qquad \text{by Theorem 1.}$$

$$\therefore \quad \bar{E}^a = \theta^a. \tag{2.1}$$

Differentiating (2.1) intrinsically with reference to $\bar{C}$, we have

$$\frac{\delta \bar{E}^a}{\delta \bar{s}} = \frac{\delta \theta^a}{\delta \bar{s}}$$

$$= \frac{\delta \theta^a}{\delta s}\frac{ds}{d\bar{s}} = (\kappa_2 \theta_{2|}{}^a - \kappa_1 E^a)\frac{ds}{d\bar{s}} \qquad [1]$$

$$= (\kappa_2 \theta_{2|}{}^a - \kappa_1 E^a)\rho.$$

But

$$\frac{\delta \bar{E}^a}{\delta \bar{s}} = \frac{\bar{\theta}^a}{\bar{\rho}}$$

where $\bar{\theta}^a$ is the unit principal-normal vector to $\bar{C}$ in V_{n+1} and $1/\bar{\rho}$ = curvature of $\bar{C}$ in V_{n+1}.

$$\therefore \quad \frac{\theta^a}{\bar{\rho}} = (\kappa_2 \theta_{2|}{}^a - \kappa_1 E^a)\rho. \tag{2.2}$$

Taking magnitudes on either side of (2.2), we have

$$\frac{1}{\bar{\rho}^2} = \frac{\kappa_1{}^2 + \kappa_2{}^2}{\kappa_1{}^2}, \text{ where } \kappa_1 = \frac{1}{\rho}$$

i.e.,

$$\frac{1}{\bar{\rho}^2} = \left(\frac{\kappa_2}{\kappa_1}\right)^2 + 1. \tag{2.3}$$

This result agrees with the well-known formula for the curvature of the spherical indicatrix of tangents of a skew curve in ordinary space.[2]

But

$$\frac{1}{\bar{\rho}^2} = \bar{\kappa}_1^2 = 1 + \bar{\kappa}_g^2,$$

since the normal curvature of $\bar{C}$ is

$$\bar{\Omega}_{ij}\bar{e}^i\bar{e}^j = -\bar{g}_{ij}\bar{e}^i\bar{e}^j = -1$$

where $\bar{e}^i$ is the unit tangent vector to $\bar{C}$ in Q_n, corresponding to the tangent vector e^i to C in V_n.

$\therefore$ (2.3) becomes

$$1 + \bar{\kappa}_g^2 = 1 + \left(\frac{\kappa_2}{\kappa_1}\right)^2$$

i.e.,

$$\bar{\kappa}_g = \frac{\kappa_2}{\kappa_1} \text{ numerically.} \tag{2.4}$$

COROLLARY 1. *$\bar{C}$ is a geodesic of Q_n if and only if C is a line of zero torsion.*

For $\bar{\kappa}_g = 0$ if and only if $\kappa_2 = 0$.

In ordinary 3-space we have the result that the spherical indicatrix of a helix is a circle and conversely.

COROLLARY 2. *The principal normal vector to C in V_{n+1} is orthogonal to that of $\bar{C}$ in V_{n+1}.*

Taking scalar products with the vector θ^α on either side of (2.2) we at once have $a_{\alpha\beta}\bar{\theta}^\alpha\theta^\beta = 0$.

COROLLARY 3. *The cosine of the angle between the tangent vector to C in V_{n+1} and the unit principal normal vector to $\bar{C}$ in V_{n+1} is numerically equal to the reciprocal of the curvature at any point of $\bar{C}$.*

i.e., $a_{\alpha\beta}\bar{\theta}^\alpha E^\beta = \bar{\rho}$.

This is obvious from (2.2).

COROLLARY 4. *If C is a curve of zero torsion, the principal normal vector to $\bar{C}$ in V_{n+1} is orthogonal to the first binormal vector to C in V_{n+1}.* Taking scalar products with the vector $\theta_{2_1}{}^{\alpha}$ on either side of (2.2), we have

$$\kappa_2 = \kappa_1\bar{\kappa}_1 (a_{\alpha\beta}\theta_{2_1}{}^{\alpha}\bar{\theta}_1{}^{\beta}).$$

$\therefore$ if $\kappa_2 = 0$, then $a_{\alpha\beta}\theta_{2_1}{}^{\alpha}\bar{\theta}_1{}^{\beta} = 0$, assuming $\kappa_1 \neq 0$.

COROLLARY 5. *The geodesic curvature at any point of $\bar{C}$ is equal to the cotangent of the angle which the principal normal vector to $\bar{C}$ makes with the first binormal vector to C,*

i.e., $\bar{\kappa}_g = \cot \omega$, where $\cos \omega = a_{\alpha\beta}\theta_{2_1}{}^{\alpha}\bar{\theta}_{1_1}{}^{\beta}$.

We have, by Corollary (4), $\kappa_2/\kappa_1 = \bar{\kappa}_1\, a_{\alpha\beta}\theta_{2_1}{}^{\alpha}\bar{\theta}_{1_1}{}^{\beta}$.

Squaring both sides, $(\kappa_2/\kappa_1)^2 = \bar{\kappa}_1{}^2 \cos^2 \omega$,

i.e., $\bar{\kappa}_g{}^2 = \bar{\kappa}_1{}^2 \cos^2 \omega$.

$\therefore$ $\bar{\kappa}_g{}^2 = (1 + \bar{\kappa}_g{}^2) \cos^2 \omega$

i.e., $\bar{\kappa}_g{}^2 \sin^2 \omega = \cos^2 \omega$.

$\therefore$ $\bar{\kappa}_g = \cos \omega / \sin \omega = \cot \omega$.

$\therefore \bar{\kappa}_g$ is constant if and only if ω is constant.

We infer that for a helix in ordinary 3-space, $\omega =$ constant and conversely.

COROLLARY 6. *If the principal normal vector to $\bar{C}$ in V_{n+1} makes an angle ϕ with the tangent vector to C in V_{n+1}, then it makes an angle $\pi/2 - \phi$ with the first binormal vector to C in V_{n+1} and conversely.*

Proof.—

$$a_{\alpha\beta}\bar{\theta}^{\alpha}\mathrm{E}^{\beta} = \cos \phi$$

But, from Corollary (3)

$$\bar{\rho} = a_{\alpha\beta}\bar{\theta}^{\alpha}\mathrm{E}^{\beta}.$$

$$\therefore \quad \bar{\kappa}_1 = 1/\bar{\rho} = \sec \phi.$$

$$\therefore \quad 1 + \bar{\kappa}_g{}^2 = \bar{\kappa}_1{}^2 = \sec^2 \phi = 1 + \tan^2 \phi.$$

$$\therefore \quad \bar{\kappa}_g = \tan \phi = \sin \phi / \cos \phi = \bar{\kappa}_1 \sin \phi.$$

$$\therefore \quad \bar{\kappa}_g = \bar{\kappa}_1 \sin \phi.$$

But by Theorem 2 and its Corollary (4),

$$\bar{\kappa}_g = \kappa_2/\kappa_1 = \bar{\kappa}_1 a_{\alpha\beta} \theta_{2|}{}^{\alpha} \bar{\theta}_{1|}{}^{\beta}.$$

$$\therefore \quad a_{\alpha\beta}\, \theta_{2|}{}^{\alpha} \bar{\theta}_{1|}{}^{\beta} = \sin \phi,$$

i.e., the principal normal vector to $\bar{C}$ in V_{n+1} makes an angle $\pi/2 - \phi$ with the first binormal vector to C in V_{n+1}.

Conversely, if the angle between $\theta_{2|}{}^{\alpha}$ and $\bar{\theta}_{1|}{}^{\alpha}$ is ψ, then the angle between $\bar{\theta}_{1|}{}^{\alpha}$ and E^{α} is $\pi/2 - \psi$.

For,

$$a_{\alpha\beta} \theta_{2|}{}^{\alpha} \bar{\theta}_{1|}{}^{\beta} = \cos \psi.$$

By Corollary (5),

$$\bar{\kappa}_g = \cot \psi.$$

$$\therefore \quad a_{\alpha\beta} \bar{\theta}_{1|}{}^{\alpha} E^{\beta} = \bar{\rho} = \frac{a_{\alpha\beta} \theta_{2|}{}^{\alpha} \bar{\theta}_{1|}{}^{\beta}}{\bar{\kappa}_g} = \frac{\cos \psi}{\cot \psi} = \sin \psi.$$

$$a_{\alpha\beta} \bar{\theta}_{1|}{}^{\alpha} E^{\beta} = \sin \psi.$$

Hence the result.

SECTION 2

Umbilical indicatrices of the principal normal and binormal vectors

Let $\theta^{\alpha} = \theta_{1|}{}^{\alpha}, \theta_{2|}{}^{\alpha}, \ldots, \theta_{n|}{}^{\alpha}$, be the unit principal normal vector, and the first, second, etc., binormal vectors at any point of C in V_{n+1}, defined by the Serret-Frenet formulæ,

$$\frac{\delta \theta_{r|}{}^{\alpha}}{\delta s} = \kappa_{r+1}\, \theta^{\alpha}{}_{r+1|} - \kappa_r \theta^{\alpha}{}_{r-1|}, \qquad (\alpha = 1, 2, \ldots, n+1)$$

$$(r = 0, 1, 2, \ldots, n)$$

where $\kappa_{n+1} = 0$, $E^q = \theta_0{}^a$, and $\kappa_1, \kappa_2, \ldots, \kappa_n$ are respectively the n curvatures corresponding to the above vectors.

Consider the locus of a point whose co-ordinates are $(\theta_{r|}{}^1, \theta_{r|}{}^2, \ldots, \theta_{r|}{}^n, \theta_{r|}{}^{n+1})$. The locus is a curve $\bar{C}_{r|}$ in the hypersurface $Q_{r|n}$ defined by $a_{\alpha\beta}\theta_{r|}{}^\alpha\theta_{r|}{}^\beta = 1$.

Exactly as in the case of the umbilical indicatrix of the tangent vector, we prove that $\bar{\Omega}_{r|ij} = -\bar{g}_{r|ij}$, where $\bar{\Omega}_{r|ij}$ is the fundamental tensor of Q_n and $\bar{g}_{r|ij}$ is the metric tensor of $\bar{C}_{r|}$.

We call the curve $\bar{C}_{r|}$, as the umbilical indicatrix of the $(r-1)$th binormal vector to C in V_{n+1}.

THEOREM 1. *The arc elements of $\bar{C}_{r|}$ and C are connected by the relation* $ds_{r|}{}^2 = (\kappa^2{}_{r+1} + \kappa_r{}^2)\, ds^2$.

Proof.—Since the tangent vector to $\bar{C}_{r|}$ is a unit vector,

$$a_{\alpha\beta}\, \theta^\alpha{}_{r|\bar{;}i}\, \bar{e}_{r|}{}^i\, \theta^\beta{}_{r|\bar{;}j}\, \bar{e}_{r|}{}^j = 1,$$

where $\bar{;}$ denotes tensor differentiation w.r.t. points of $\bar{C}_{r|}$.

$$a_{\alpha\beta}\, \frac{\delta\theta^\alpha{}_{r|}}{\delta s_{r|}} \cdot \frac{\delta\theta^\beta{}_{r|}}{\delta s_{r|}} = 1.$$

i.e., $$a_{\alpha\beta}\, \frac{\delta\theta^\alpha{}_{r|}}{\delta s}\, \frac{\delta\theta^\beta{}_{r|}}{\delta s} \left(\frac{ds}{ds_{r|}}\right)^2 = 1.$$

i.e., $$a_{\alpha\beta}\, (\kappa_{r+1}\, \theta^\alpha{}_{r+1|} - \kappa_r\, \theta^\alpha{}_{r-1|})\, (\kappa_{r+1}\, \theta^\beta{}_{r+1|} - \kappa_r\, \theta^\beta{}_{r-1|}) \times \left(\frac{ds}{ds_{r|}}\right)^2 = 1.$$

$$\therefore \quad ds_{r|}{}^2 = (\kappa^2{}_{r+1} + \kappa_r{}^2)\, ds^2.$$

THEOREM 2. *The $(r-1)$th binormal vector to C in V_{n+1} is orthogonal to the unit tangent vector to $\bar{C}_{r|}$.*

Proof.—The components of the unit tangent vector to $\bar{C}_{r|}$ are given by

$$\bar{E}^\alpha{}_{r|} = \frac{\delta\theta^\alpha{}_{r|}}{\delta s}\, \frac{ds}{ds_{r|}} = (\kappa_{r+1}\theta^\alpha{}_{r+1|} - \kappa_r\theta^\alpha{}_{r-1|})\, \frac{ds}{ds_{r|}} \tag{3.1}$$

Obviously, $\theta_{r|} \cdot \bar{E}_{r|} = 0$. Hence the result.

Let $\Phi_{r|1}{}^{\alpha}$ be the unit principal normal vector to $\bar{C}_{r|}$ in V_{n+1}, and $\bar{\kappa}_{1/r} = 1/\bar{\rho}_{1|r}$, the first curvature of $\bar{C}_{r|}$ in V_{n+1}.

$$\frac{\Phi_{r|1}{}^{\alpha}}{\bar{\rho}_{1|r}} = \frac{\delta \bar{E}_{r|}{}^{\alpha}}{\delta \bar{s}_{r|}} = \frac{\delta}{\delta \bar{s}_{r|}} \left(\frac{\delta \theta_{r|}{}^{\alpha}}{\delta s} \frac{ds}{d\bar{s}_{r|}} \right)$$

$$= \frac{\delta}{\delta s} \left[\kappa_{r+1} \theta^{\alpha}{}_{r+1|} - \kappa_r \theta^{\alpha}{}_{r-1|} \right] \left(\frac{ds}{ds_{r|}} \right)^2$$

$$+ \tfrac{1}{2} \left(\kappa_{r+1} \theta^{\alpha}{}_{r+1|} - \kappa_r \theta^{\alpha}{}_{r-1|} \right) \frac{d}{ds} \left(\frac{1}{\kappa_{r+1}{}^2 + \kappa_r{}^2} \right).$$

For $r = 2$, we have the umbilical indicatrix of the unit first binormal vector.

$$\bar{\kappa}_{1|2} \Phi_{2|1}{}^{\alpha} = \left[\frac{\delta}{\delta s} \left(\kappa_3 \theta_3{}^{\alpha} \right) - \kappa_2{}' \theta_1{}^{\alpha} - \kappa_2 \left(\kappa_2 \theta_2{}^{\alpha} - \kappa_1 E^{\alpha} \right) \right] \frac{1}{\kappa_3{}^2 + \kappa_2{}^2}$$

$$+ \tfrac{1}{2} \left(\kappa_3 \theta_3{}^{\alpha} - \kappa_2 \theta_1{}^{\alpha} \right) \frac{d}{ds} \left(\frac{1}{\kappa_3{}^2 + \kappa_2{}^2} \right).$$

If C is a curve in ordinary 3-space,

$$\kappa_3 = 0 \text{ and } \kappa_2{}^2 = \left(\frac{d\bar{s}}{ds} \right)^2,$$

so that

$$\frac{\Phi_{2|1}{}^{\alpha}}{\bar{\rho}_{1|2}} = \frac{1}{\kappa_2{}^2} \left[-\kappa_2{}' \theta_1{}^{\alpha} - \kappa_2{}^2 \theta_2{}^{\alpha} + \kappa_2 \kappa_1 E^{\alpha} - \tfrac{1}{2} \kappa_2 \theta_1{}^{\alpha} \cdot \left(\frac{-2\kappa_2{}'}{\kappa_2{}^3} \right) \right]$$

where $\kappa_2{}' = \delta \kappa_2 / \delta s$.

$$\therefore \quad \frac{\Phi_{2|1}{}^{\alpha}}{\bar{\rho}_{1|2}} = -\frac{1}{\kappa_2} \left[\kappa_2 \theta_2{}^{\alpha} - \kappa_1 E^{\alpha} \right]$$

$$\therefore \quad \frac{1}{\bar{\rho}_{1|2}{}^2} = \frac{1}{\kappa_2{}^2} \left(\kappa_2{}^2 + \kappa_1{}^2 \right) = \left(\frac{\kappa_1}{\kappa_2} \right)^2 + 1.$$

This agrees with the known formula for the curvature of the spherical indicatrix of the binormals of a skew curve in ordinary space (2).

$$\therefore \quad 1 + \kappa_{g|2}{}^2 = 1 + \left(\frac{\kappa_1}{\kappa_2} \right)^2$$

i.e.,

$$\bar{\kappa}_{g|2} = \frac{\kappa_2}{\kappa_2}.$$

$\therefore \bar{\kappa}_g$ is constant if and only if κ_1/κ_2 is constant.

Expressed in words, this means, *the binormal indicatrix of a helix in ordinary 3-space is a circle and conversely.*

THEOREM 3. *If the unit principal normal vector to $\bar{C}_{r1}$ is co-directional with the unit $(r-1)$th binormal vector to $\bar{C}$, then $\bar{C}_{r1}$, the image of C, is a geodesic and conversely.*

$$\frac{\Phi_{r11}{}^{a}}{\rho_{11r}} = [\kappa'_{r+1}\theta_{r+11}{}^{a} + \kappa_{r+1}(\kappa_{r+2}\theta_{r+21}{}^{a} - \kappa_{r+1}\theta_{r1}{}^{a}) - \kappa'_{r}\theta_{r-11}{}^{a}$$

$$- \kappa_{r}(\kappa_{r}\theta_{r1}{}^{a} - \kappa_{r-1}\theta_{r-21}{}^{a})] \frac{1}{\kappa_{r+1}{}^{2} + \kappa_{r}{}^{2}}$$

$$+ \tfrac{1}{2}[\kappa_{r+1}\theta_{r+11}{}^{a} - \kappa_{r}\theta_{r-11}{}^{a}] \frac{d}{ds}\left(\frac{1}{\kappa_{r+1}{}^{2} + \kappa_{r}{}^{2}}\right)$$

$$\frac{a_{\alpha\beta}\Phi_{r11}{}^{\alpha}\theta_{r1}{}^{\beta}}{\rho_{11r}} = -\frac{\kappa_{r+1}{}^{2} + \kappa_{r}{}^{2}}{\kappa_{r+1}{}^{2} + \kappa_{r}{}^{2}} = -1.$$

But

$$(a_{\alpha\beta}\,\Phi_{r11}{}^{\alpha}\theta_{r1}{}^{\beta})^{2} = \rho^{2}{}_{11r}$$

$$= 1 + \bar{\kappa}^{2}{}_{g1r},$$

since normal curvature of $\bar{C}_{r1}$ at any point

$$= \bar{\Omega}_{r1ij}\bar{e}_{r1}{}^{i}\bar{e}_{r1}{}^{j} = -\bar{g}_{r1ij}\bar{e}_{r1}{}^{i}\bar{e}_{r1}{}^{j} = -\pm 1.$$

$$\therefore\ \bar{\kappa}_{g1r} = 0 \text{ if and only if } a_{\alpha\beta}\Phi_{r11}{}^{\alpha}\theta_{r1}{}^{\beta} = 1.$$

Hence the theorem.

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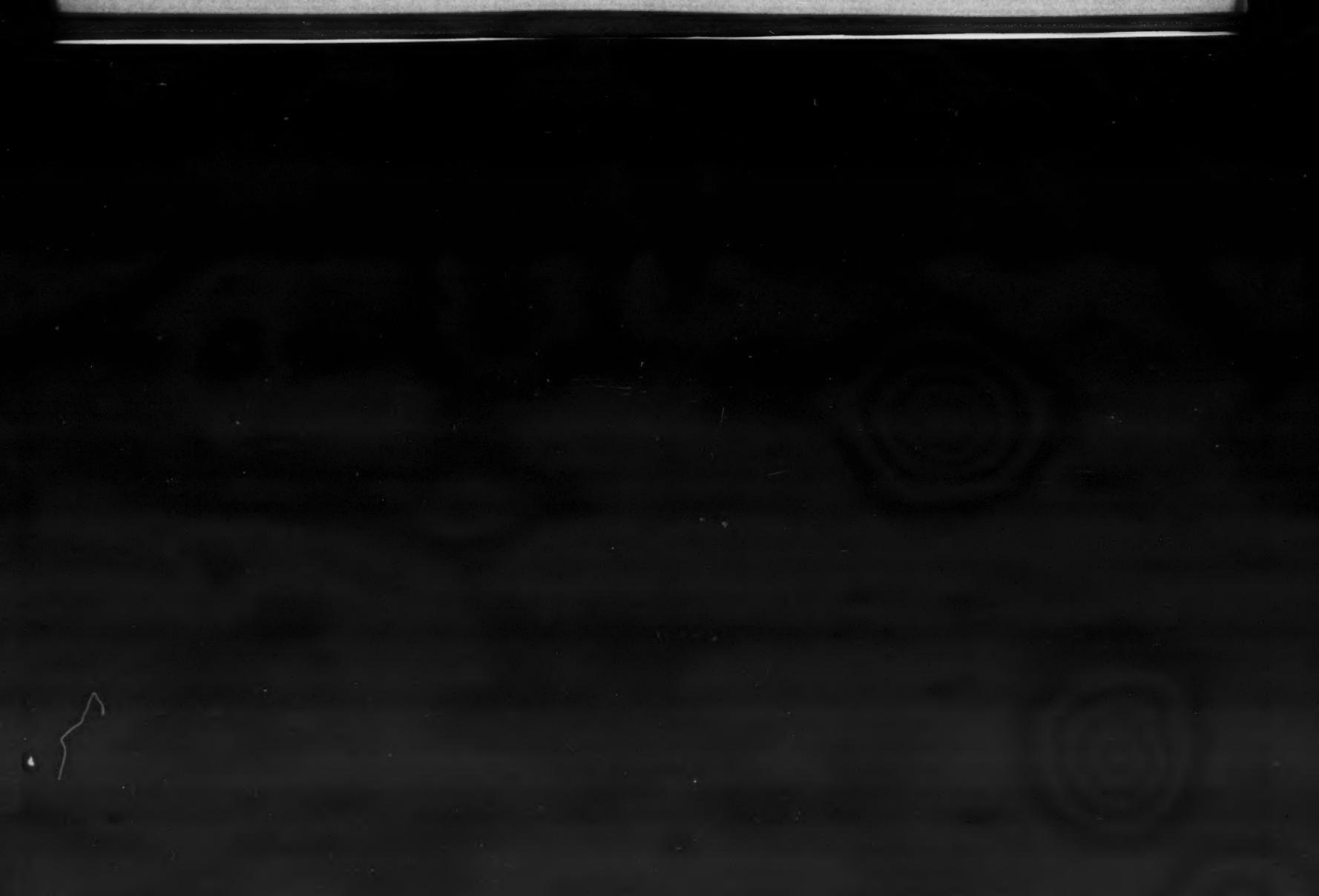
ERRATA

Vol. XLIV, Section A, No. 4, *Proc. Indian Acad. Sci.*,
Oct. 1956, p. 195, Fig. 1

In Fig. 1, the three pulses, namely the fast coincidence output and the outputs from each of the two single channel pulse analysers, feeding the first triple coincidence unit should also have been shown to be feeding the second triple coincidence unit for counting chance coincidences. The limiter outputs should not have been shown feeding the triple coincidence circuit.



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